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1938-1

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Power from the Sun: the Advent of Mesoscopic Solar Cells

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Power from the Sun
The Advent of Mesoscopic Solar Cells

JOINT ICPT-KFAS Workshop on Nanoscience for Solar Energy Conversion
Trieste Italy October 27-29, 2008

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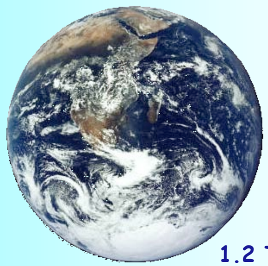
Renewable energy sources need to cover the supply gap

Solar
100'000 TW at Earth surface
10,000 TW (technical value)
(1.5 hr sunlight globally = 13 TW-yr)

energy gap
~ 14 TW by 2050
~ 33 TW by 2100

Wind
14 TW



Biomass
5-7 TW
all cultivatable land not used for food

Tide/Ocean Currents
0.7 TW

Hydroelectric
1.2 TW technically feasible
0.6 TW installed capacity

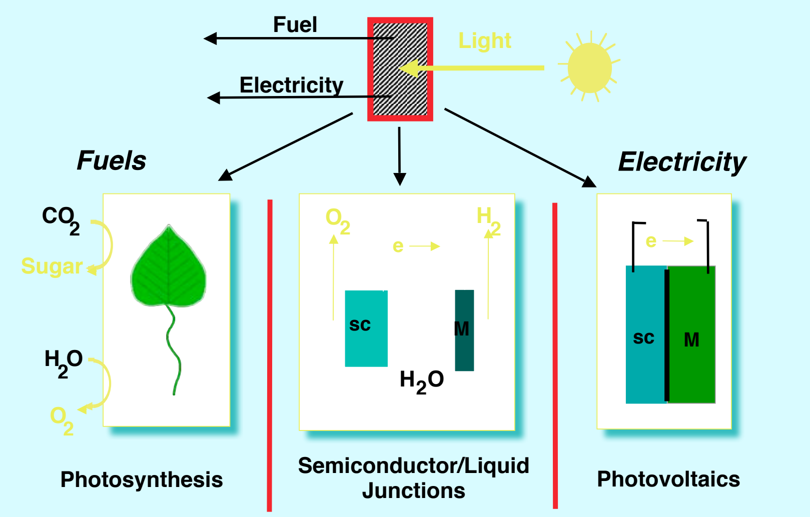
Geothermal
1.9 TW

from Nate Lewis

THE SOLAR CHALLENGE

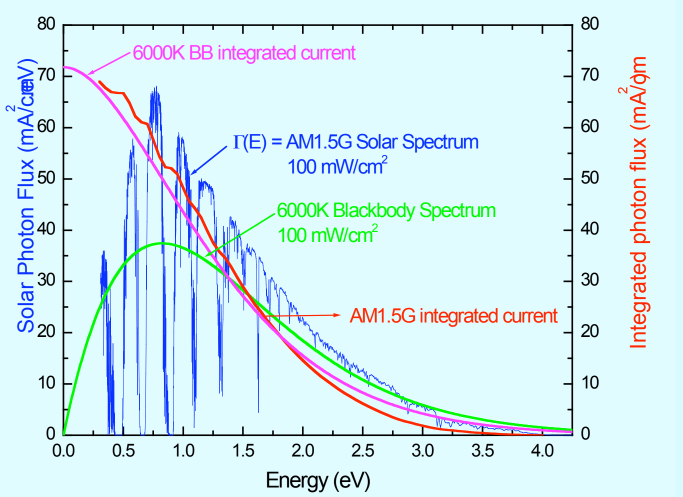
- **With a projected global population of 12 billion by 2050 coupled with moderate economic growth, the total global energy consumption is estimated to be ~28 TW. Current global use is ~11 TW.**
- **To cap CO_2 at 550 ppm (twice the pre-industrial level), most of this additional energy needs to come 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.**

Quantum Energy Conversion Strategies

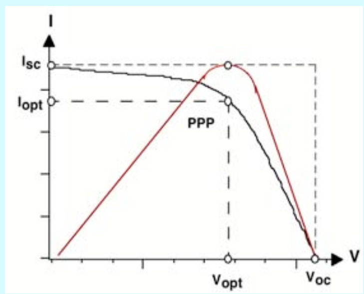


THE SOLAR RESOURCE

Solar Spectrum and Available Photocurrent



Correct device characterisation is essential

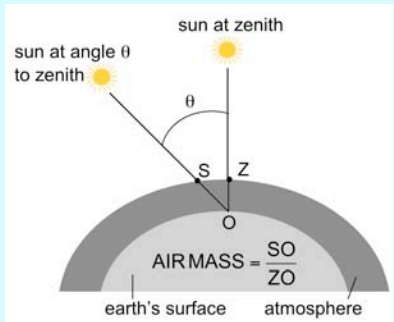


Power conversion efficiency

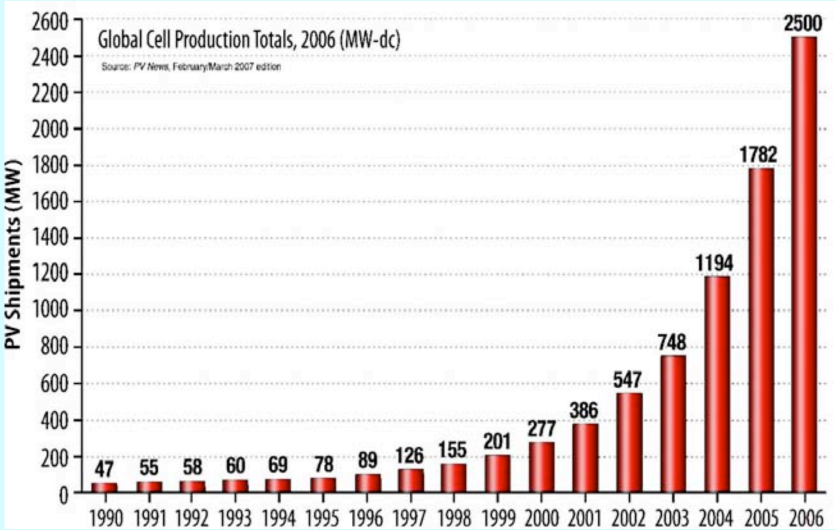
$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{SC} \cdot U_{OC} \cdot FF}{P_{in}}$$

Characterisation Standard:

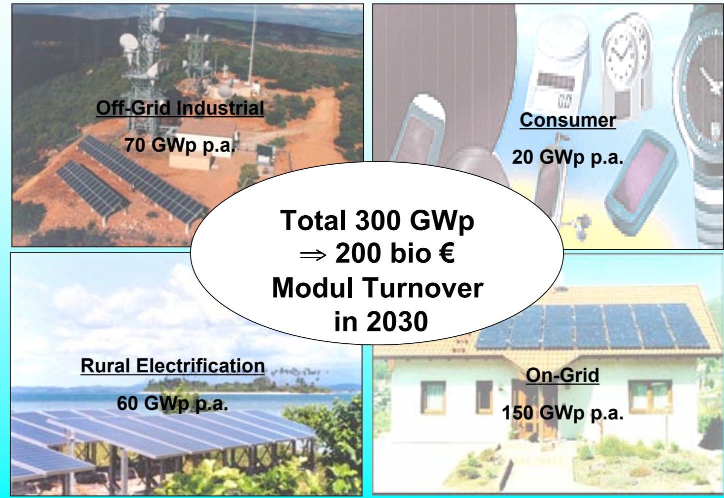
- **intensity of 1000 W/m²**
- **spectral power distribution corresponding to AM1.5 ≡ 1Sun**
- **temperature 298 K**



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 €

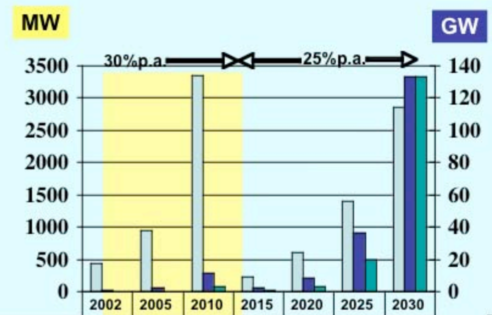


Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

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

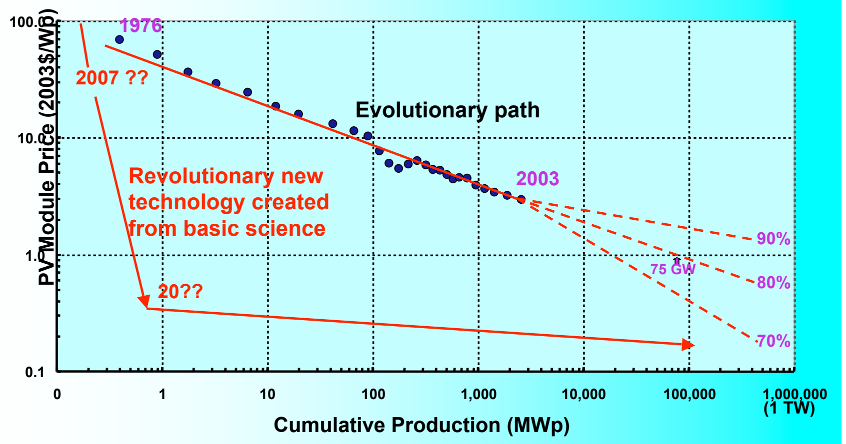


	2002	2005	2010	2015	2020	2025	2030
c-Si	430	950	3340				
thin film	20	50	290				
"New Concepts"			70				
c-Si				9	24	56	114
thin film				2	8	36	133
"New Concepts"				1	3	20	133

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

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

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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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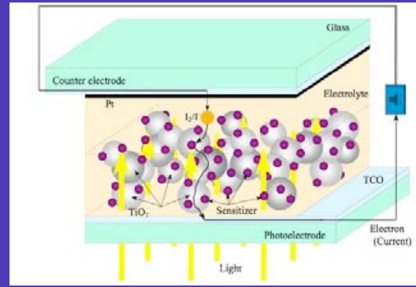
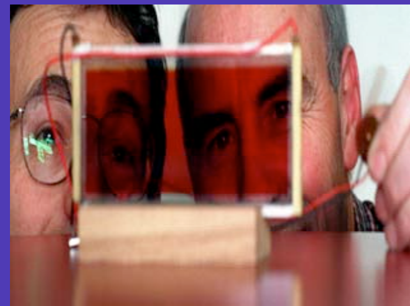
† To whom correspondence should be addressed.





NATURE PHOTONICS WEB RELEASE OCTOBER 2008

Bifacial dye-sensitized solar cells based on an ionic liquid electrolyte

SEIGO ITO[1,2]*, SHAIK M. ZAKEERUDDIN[2], PASCAL COMTE[2], PAUL LISKA[2], DAIBIN KUANG[2] AND MICHAEL GRÄTZEL[2]

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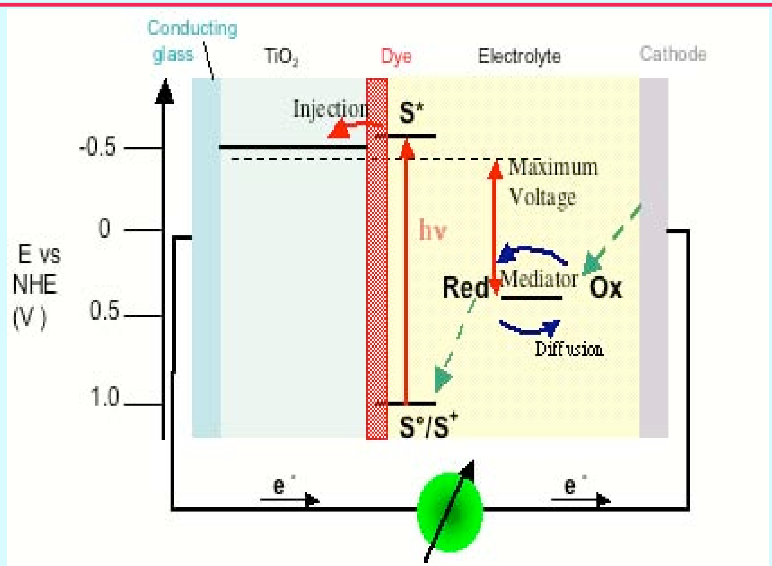
*e-mail: itou@eng.u-hyogo.ac.jp

Published online: 19 October 2008; doi:10.1038/nphoton.2008.224

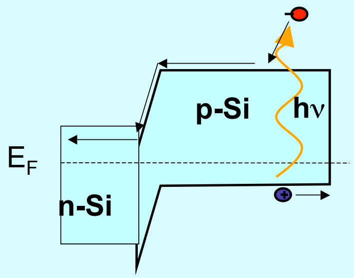
Solar energy is a promising solution to global energy-related problems because it is clean, inexhaustible and readily available. However, the deployment of conventional photovoltaic cells based on silicon is still limited by cost, so alternative, more cost-effective approaches are sought. Here we report a bifacial dye-sensitized solar cell structure that provides high photo-energy conversion efficiency (~6%) for incident light striking its front or rear surfaces. The design comprises a highly stable ruthenium dye (Z907Na) in combination with an ionic-liquid electrolyte and a porous TiO_2 layer. The inclusion of a SiO_2 layer between the electrodes to prevent generation of unwanted back current and optimization of the thickness of the TiO_2 layer are responsible for the enhanced performance.

The dye sensitized solar cell (DSC) is the only photovoltaic cell using amolecules that generated charge carriers after photo-excitation without the need for excitonic transport

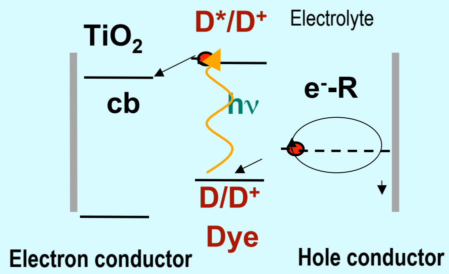


Dye sensitized solar cells separate light absorption from carrier transport

p-n junction photovoltaic cells



dye sensited solar cells DSC



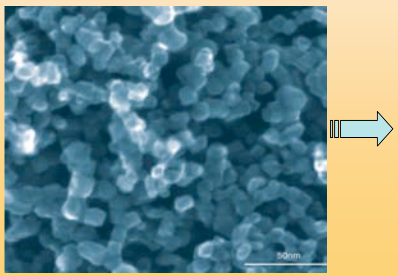
Charge separation by electric field at the p-n junction

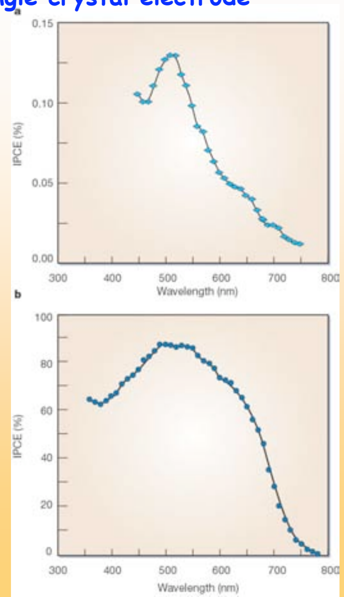
Charge separation by kinetic competition as in photosynthesis

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

single crystal of anatase

Nanocrystalline anatase film





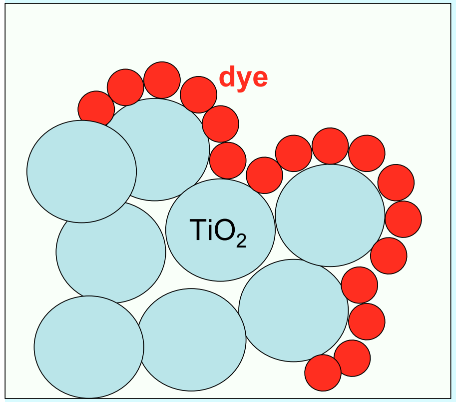
Dye sensitized nanocrystals achieve quantitative conversion of photons into electric current

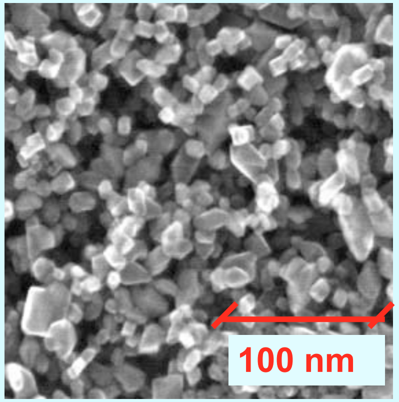
The incident photon to electrical current conversion efficiency (external quantum efficiency) can reach close to 100 %

$$\eta = \eta_{abs} {}^{*} \Phi_{inj} {}^{*} \eta_{coll}$$

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

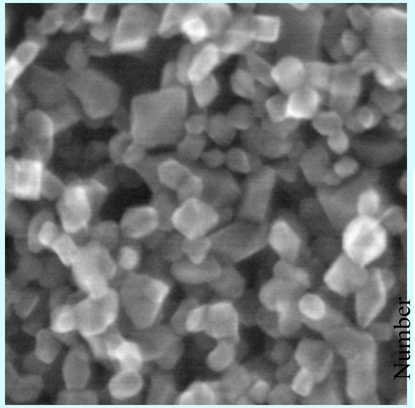
The collection of photo-generated electrons by the nanoparticle array is quantitative

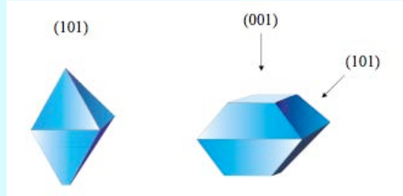


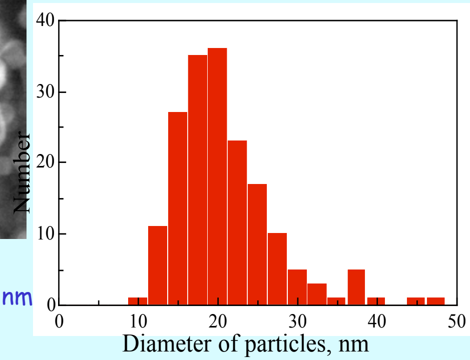


The electrons ad holes move in different phases and are separated by a phase boundary retarding their recombination

Titania (anatase) nanoparticles show well facetted surfaces with preferred (101) orientation

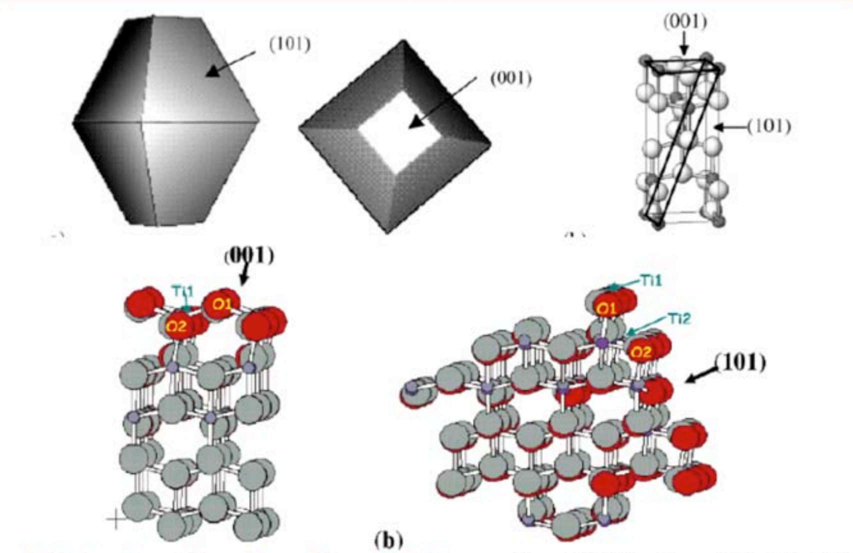






The average particle size is ca 20 nm

(101) and (001) facets prevail on TiO2 anatase nanocrystals

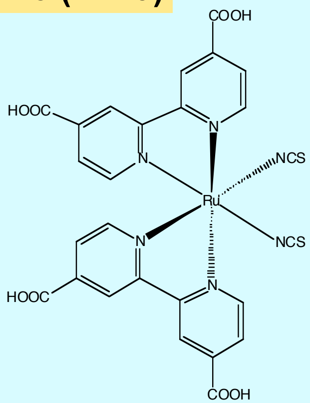


Red: atomic positions after surface relaxation

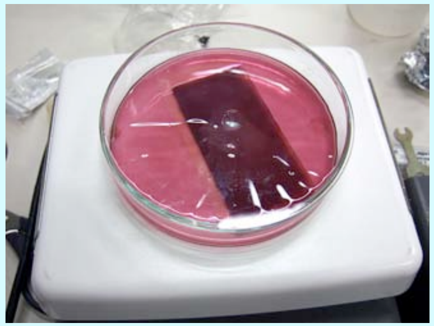
Olson et.al J.Phys.Chem. 2006, 110 ,9995

Ruthenium complexes are widely used as sensitizers due to their extraordinary performance and excellent stability

N3 (N719)

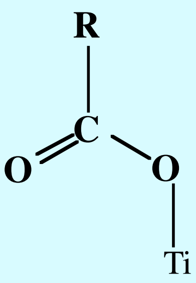


Spontaneous uptake of N3 sensitizer by a nanocrystalline TiO2 film supported on conducting glass

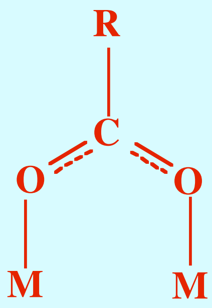


Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. J. American Chemical Society (1993), 115(14), 6382-90.

Anchoring of the carboxylate groups occurs by unidentate and bridging bidentate coordination to surface titanium ions



Unidentate

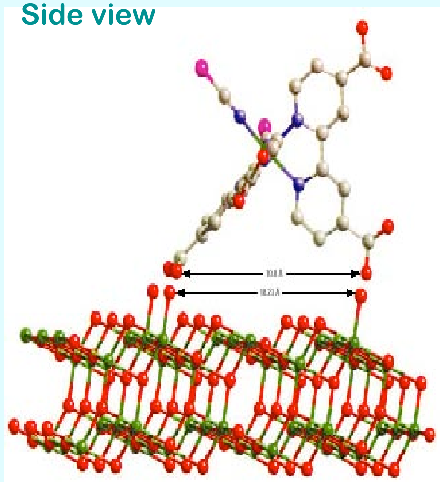


Bridging bidentate

25

The RuL_2 $(NCS)_2$ sensitizer is anchored to the (101) TiO2 anatase surface through coordinative binding of two carboxyl groups to surface titanium ions.

Side view



Top view

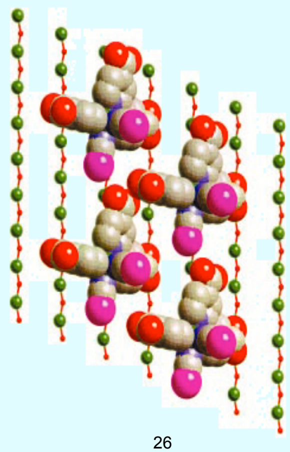


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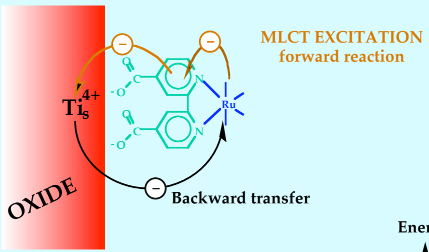
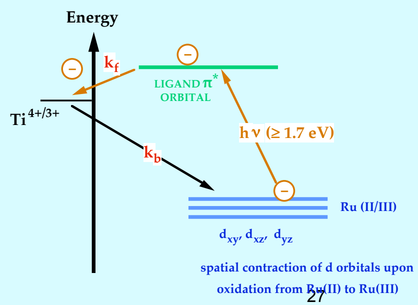
Photo Induced Heterogeneous Electron Transfer Cycle





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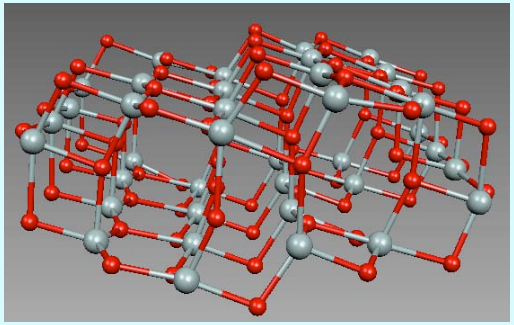
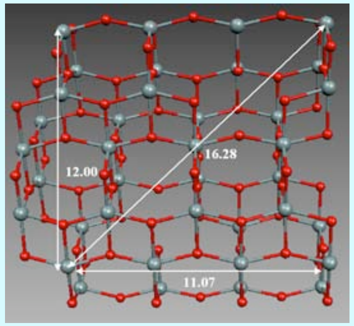
Time dependent DFT Modeling of TiO_2 nanoparticles produces correct band gap in water

Stoichiometric anatase $Ti_{38}O_{76}$ cluster of nanometric dimensions exposing (101) surfaces



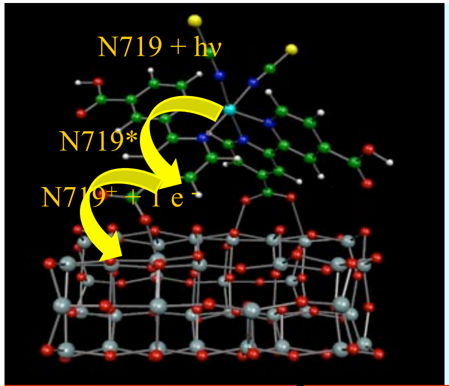


B3LYP/3-21g* : 3.20 eV, B3LYP/DZVP: 3.13 eV

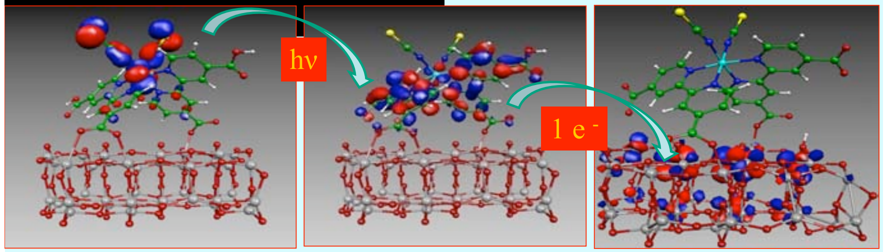
Experimental gap in aqueous solutions: 3.20 – 3.30 eV

28

F. De Angelis, A. Tilocca, A. Selloni *J. Am. Chem. Soc.* 2004, *126*, 15024



Photoinduced interfacial electron injection occurs on a femtosecond time scale

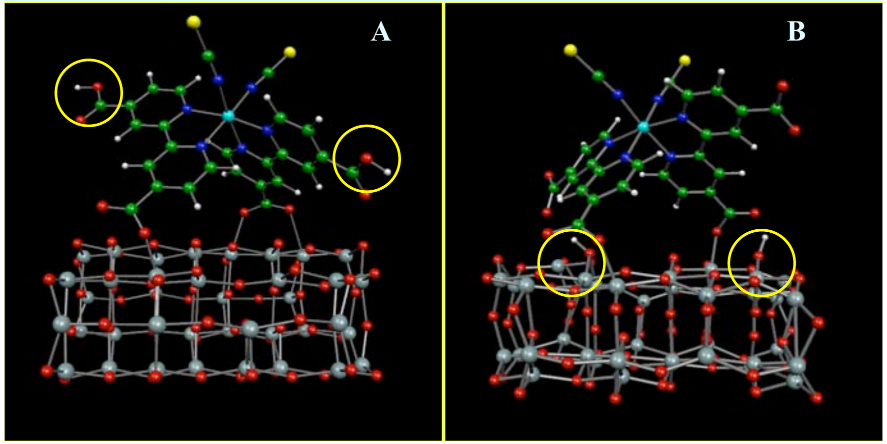


F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel *J. Am. Chem. Soc.* 2007

MD and DFT calculations provide important insight into sensitizer interaction with surface

Two prototypical configurations of N719/TiO_2 were examined:

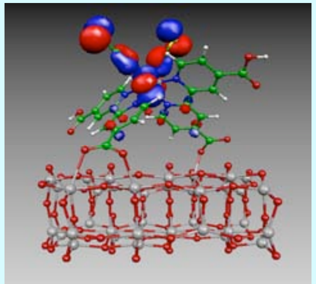
(A The two protons are located on the dye or (B) on the TiO_2



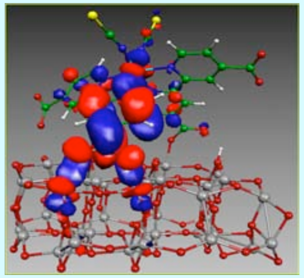
Electron injection from excited N 719 sensitizer in the conduction band of TiO2 is asssisted by surface protonation

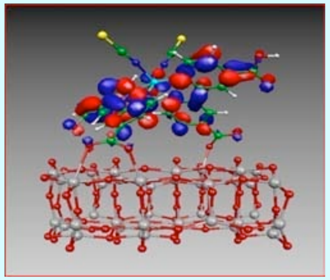
De Angelis, . Fantacci, S.; Selloni, A.; Nazeeruddin, M. K.; Graetzel, M JACS (2007), 129(46), 14156-14157

HOMO



B



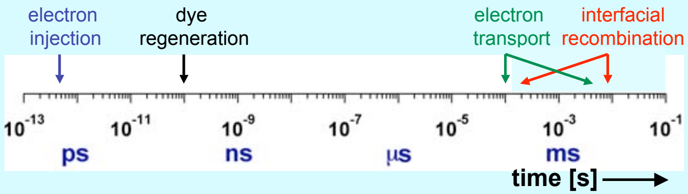


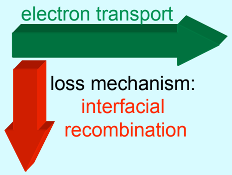
A

LUMO: 2 protons transferred from N719 to TiO2 nanoparticle

LUMO: 2 protons remain on N719

Dynamic Competition





Competition ⇒

Electron diffusion length

$$L_n = \sqrt{D_n \cdot \tau_n}$$

τ_n: electron lifetime

D_n: electron diffusion coefficient

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}:

$D = 10^{-4}$ cm²/s, τ = 1 s, L = 100 µm

The film thickness is less than 30 micrometer

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 %.

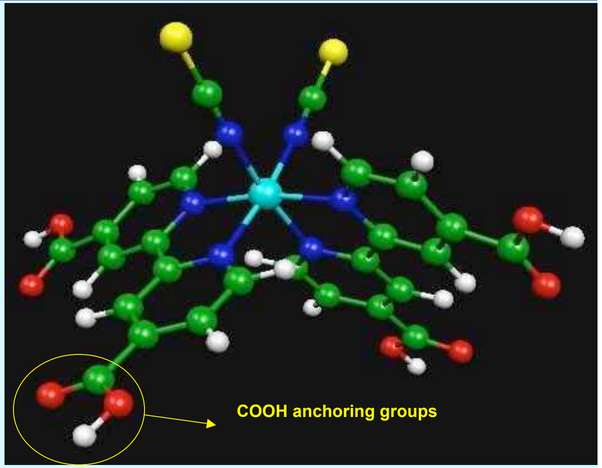
Chiba, Y., Islam, A.; Watanabe, Y; Komiya, R.; Koide, N.; Han, L..
Dye-sensitized solar cells with conversion efficiency of 11.1%.
Japanese Journal of Applied Physics, Part 2: Letters & Express Letters (2006), 45(24-28),

Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- redox active ionic liquids
- tandem devices

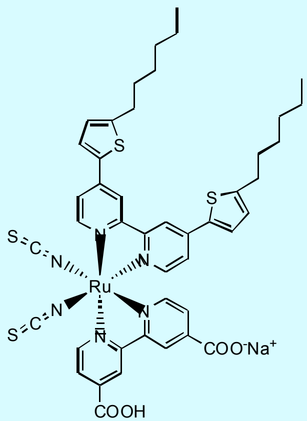
the work horse of the DSC is the N3 (or N719) ruthenium dye,

Dr. Md. K. Nazeeruddin
Senior Scientist and
Adjoint scientifique
LPi/EPFL Lausanne

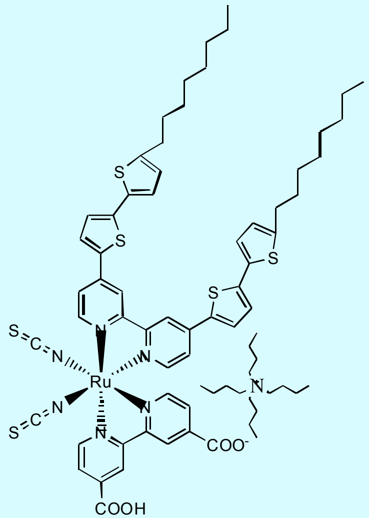


Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. J. American Chemical Society (1993), 115(14), 6382-90.

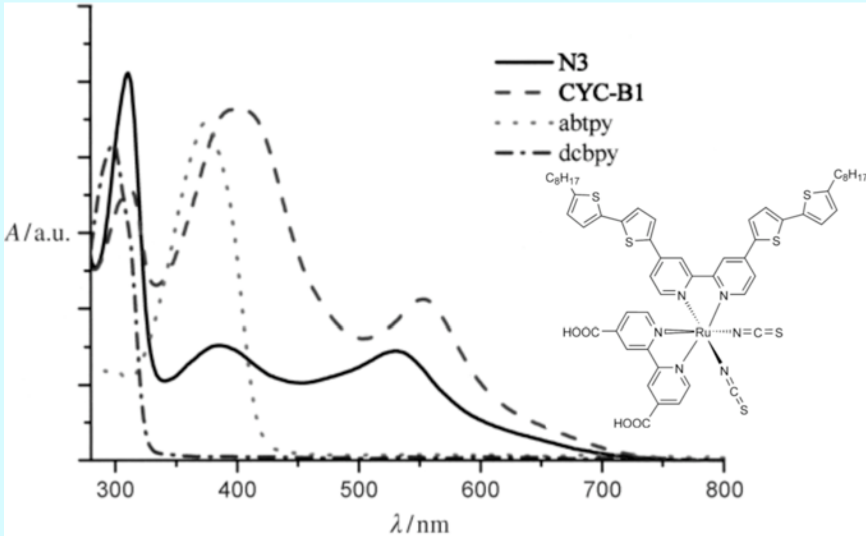
C101



Z991



Takeru. B



Chen, Chia-Yuan; Wu, Shi-Jhang; Wu, Chun-Guey; Chen, Jian-Ging; Ho, Kuo-Chuan
Angew, Chem,, Int.Ed. (2006), 45, 5822-5825.

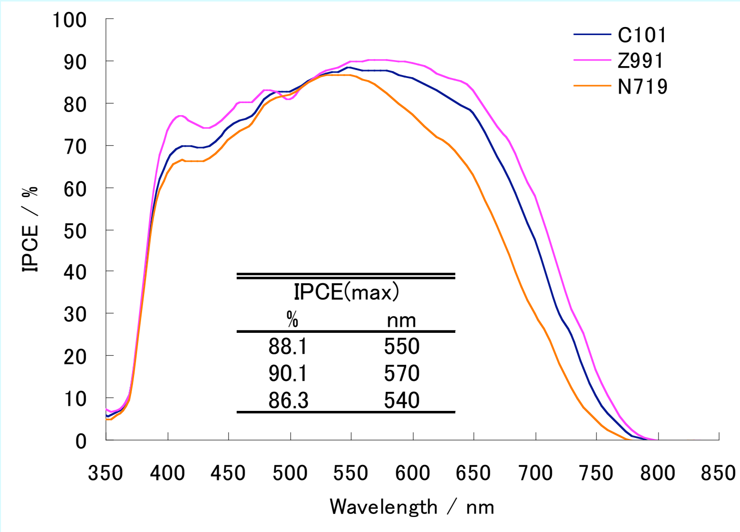
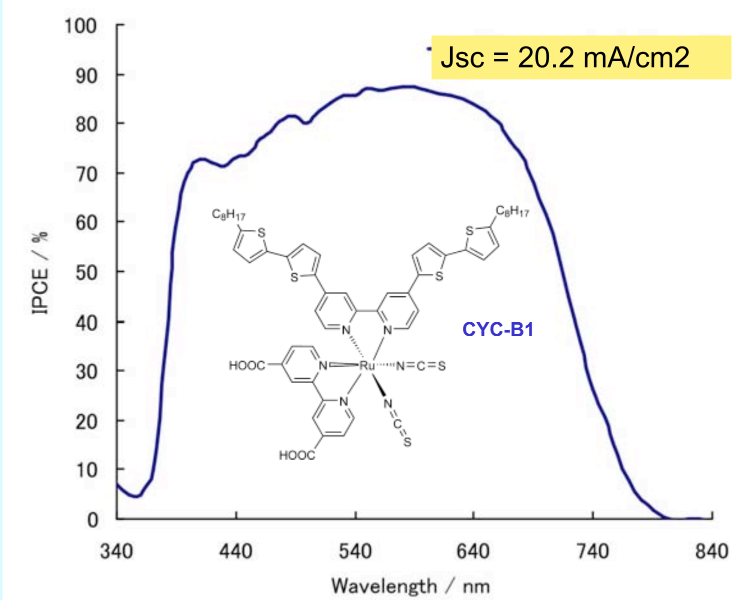


Figure. Comparison of IPCE curve with Z960 electrolyte from C101(blue), Z991(pink) and N719(orange) sensitizer, respectively. 8.4(DSL18)+4.8(CCIC400) TiO2 film was used as semiconductor.

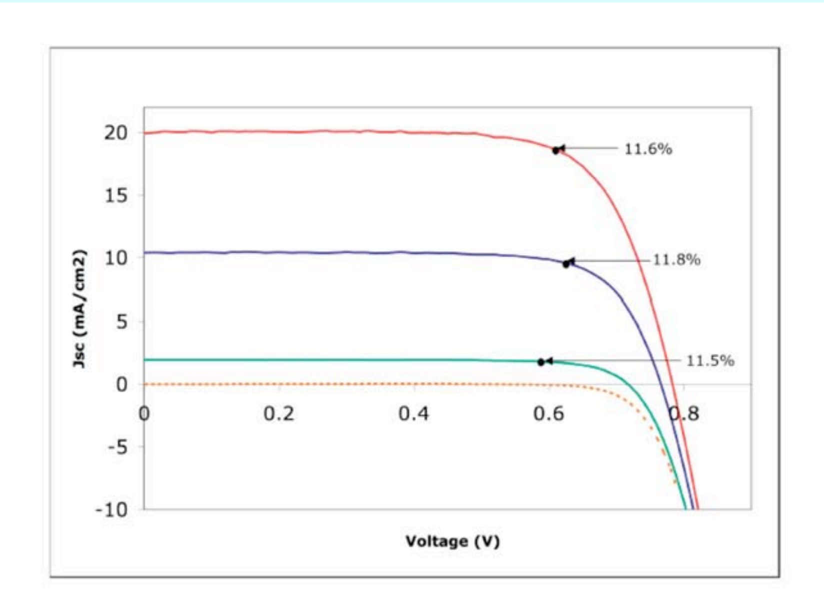
41

Takeru. B

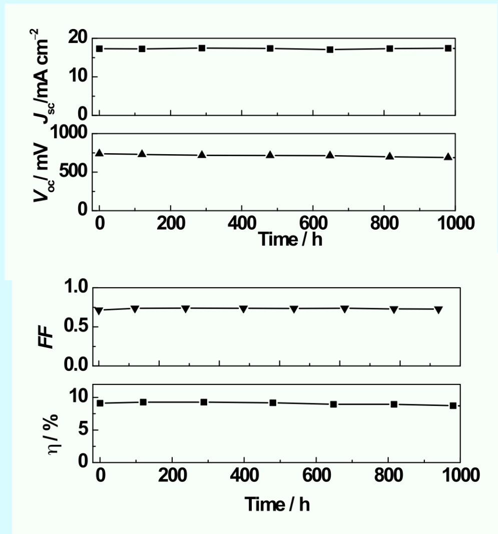


In collaboration with Professor; Wu, Chun-Guey;

Department of Chemistry, National Central University, Jung-Li, Taiwan

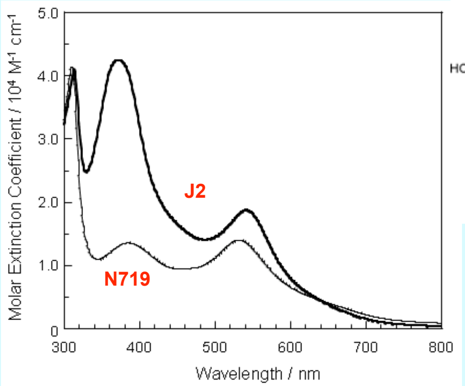


The C101 sensitizer maintains outstanding stabiity at efficieny levels over 9 percent under light soaking at 60°C with a non-volatile electrolyte



Shimane Institute for Industrial Technology

The New Dye “J2” developed by SIIT



Adsorption spectra of J2 and N719

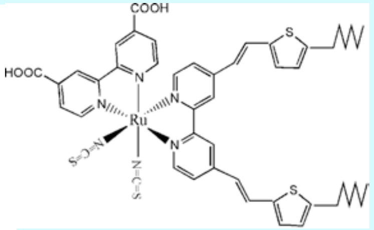
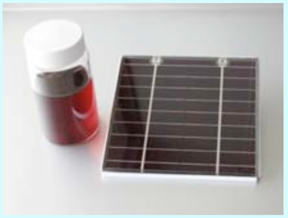
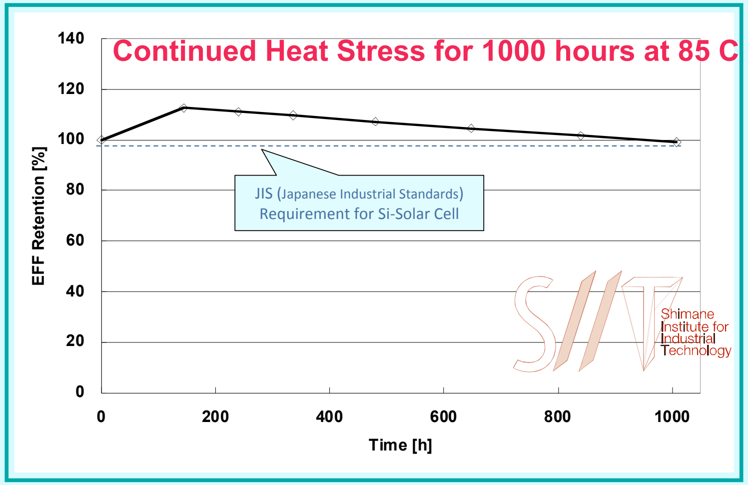


Fig.2 Structure of J2 dye



Courtesy Professor Katsumi Yoshino

High temperature stability reached on the module scale

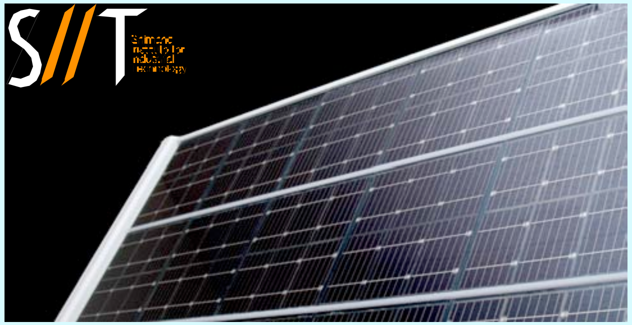


Courtesy A. Yoshino, Shimane Institute of Technology

Development of Large Size Dye-Sensitized Solar Cell Modules with High Temperature Durability

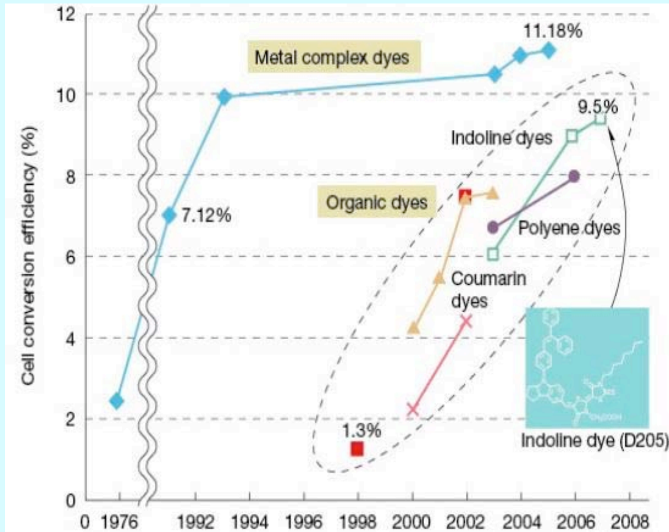
Shuji NODA, Kazuhide NAGANO, Eiji INOUE,
Toshio EGI, Takeshi NAKASHIMA, Naoto IMAWAKA,
Masahiro KANAYAMA, Shiro IWATA, Kunihiro TOSHIMA, Keiko NAKADA
and Katsumi YOSHINO

Shimane Institute for Industrial Technology (JAPAN)



The Shimane Institute for Industrial Technology (SIIT) is an organization whose purpose is to provide technical assistance to corporations in Shimane Prefecture that carry out pioneering research and development for the creation of new industries, and to work for the improvement of industrial competitiveness.

Organic dyes are catching up in conversion efficiency



Source: *Tetsuo Nozawa Nikkei Electronics Asia* -- July 2008,

Organic push-pull sensitizers are catching up

J|A|C|S
A R T I C L E S

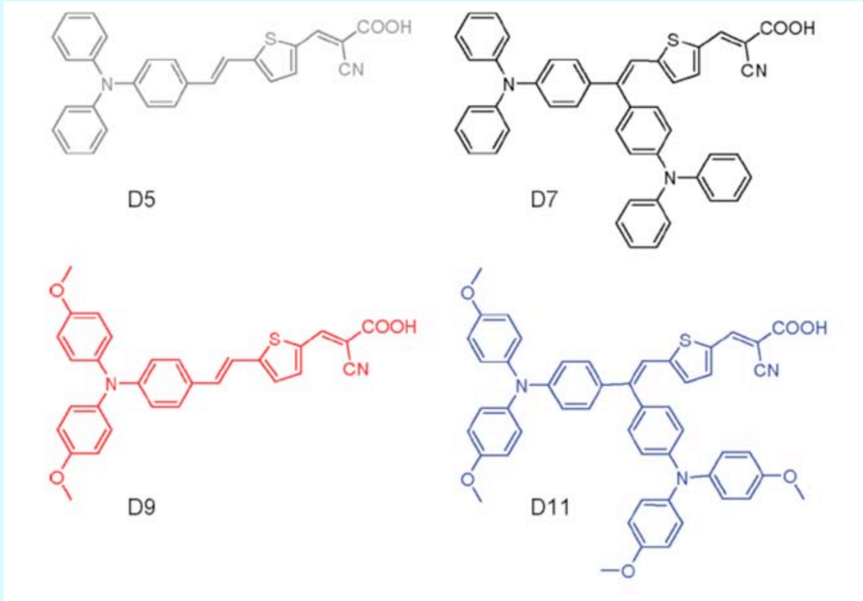
Published on Web 04/18/2008

Molecular Engineering of Organic Sensitizers for Dye-Sensitized Solar Cell Applications

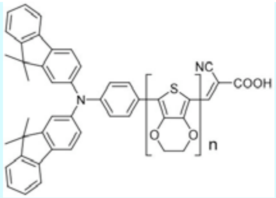
Daniel P. Hagberg,† Jun-Ho Yum,§ HyoJoong Lee,§ Filippo De Angelis,‖ Tannia Marinado,‡ Karl Martin Karlsson,† Robin Humphry-Baker,§ Licheng Sun,*,† Anders Hagfeldt,*,‡ Michael Grätzel,§ and Md. K. Nazeeruddin*,§

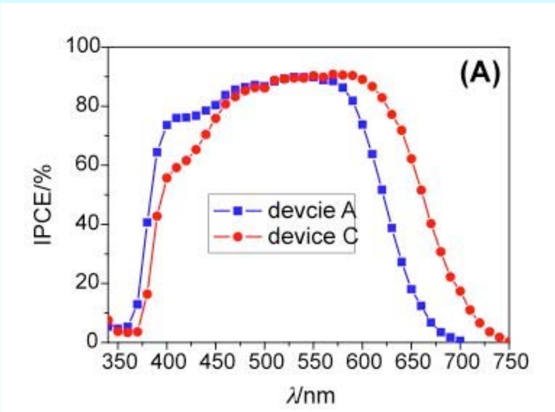
Organic Chemistry and Physical Chemistry, Center of Molecular Devices, Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden, Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, and Istituto CNR di Scienze e Tecnologie Molecolari (ISTM), c/o Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, I-06123, Perugia, Italy

Received January 4, 2008; E-mail: lichengs@kth.se; hagfeldt@kth.se; mdkhaja.nazeeruddin@epfl.ch



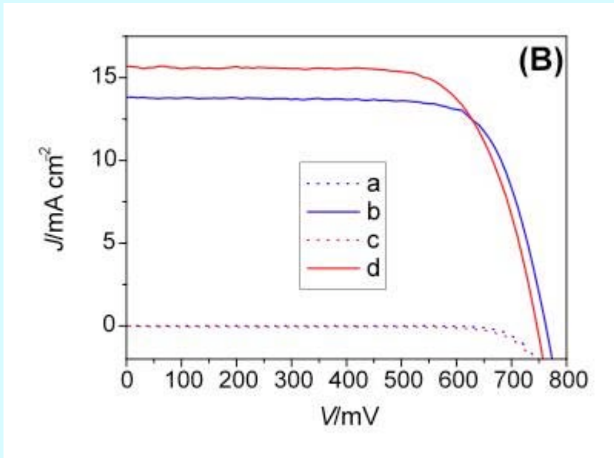
D–Π–A Dyes gaining red response





A: D-204 (n=1)
C: D-205 (n=2)

In collaboration with Peng Wang CAS Changchun

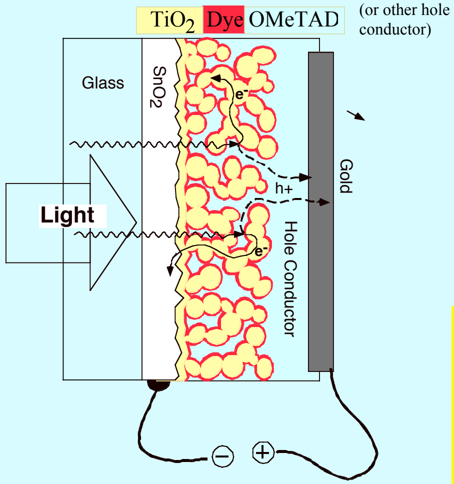


Red: D-204 , blue: D205

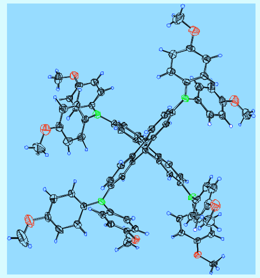
Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- redox active ionic liquids
- tandem devices

Solid State Dye Sensitized PV cell



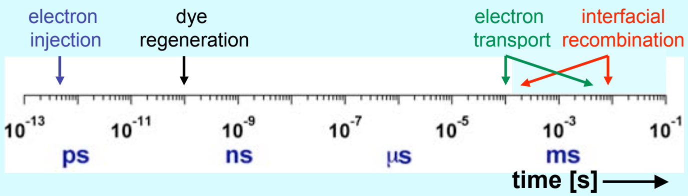
Spiro-OMeTAD

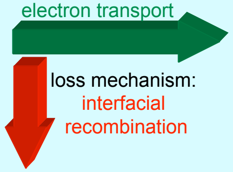


Glass transition temperature: *121 °C*
Melting Point: *246 °C*
Work function: *4.9 eV*
(CV in CH_2Cl_2. *110 mV* vs. Fc/Fc^+)
Absorption maximum neutral:
λ_{max}=*372 nm* (ε=*40100*)
Radical cation:
λ_{max}=*511 nm* (ε=*37400*)

Mobility ~ 1 x10^{-4} V/cm

Dynamic Competition





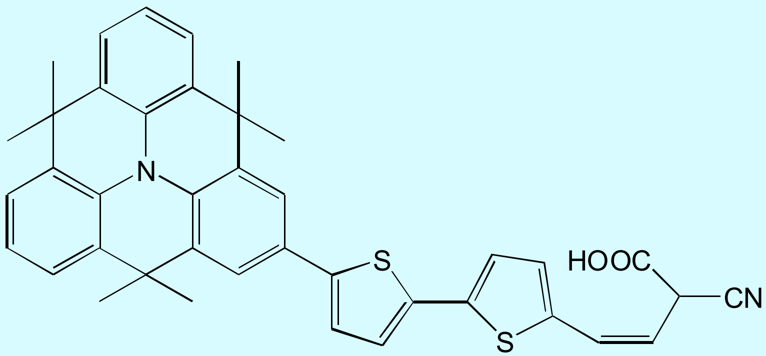
Competition ⇒

Electron diffusion length

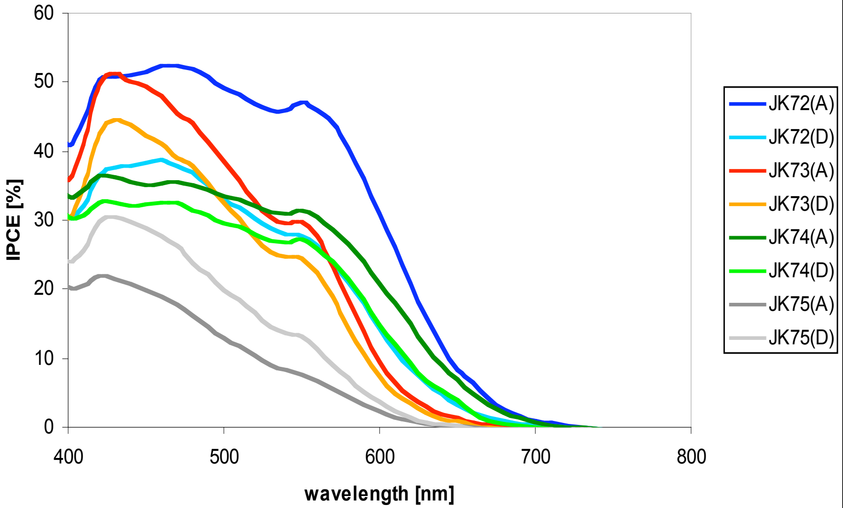
$$L_n = \sqrt{D_n \cdot \tau_n}$$

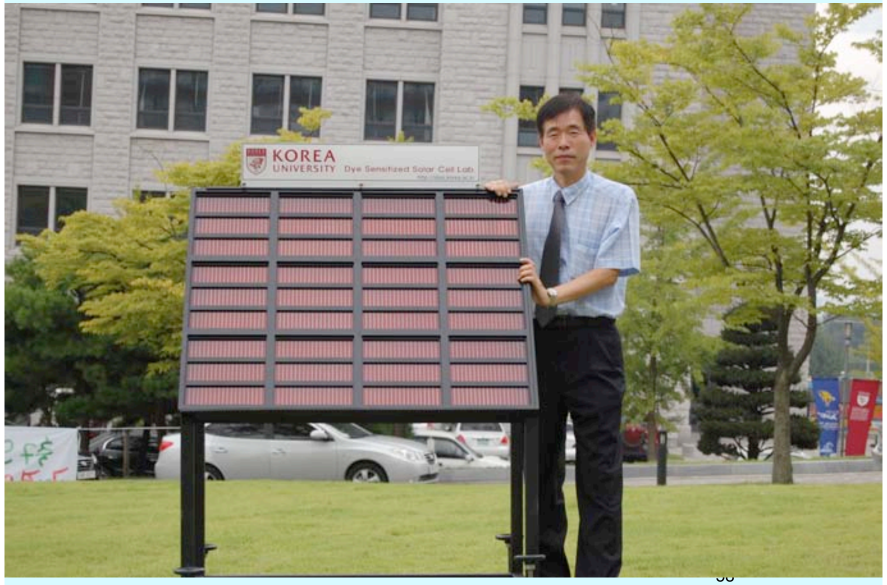
τ_n: electron lifetime
D_n: electron diffusion coefficient

JK72



Gain of red response in photocurrent by formation of JK72 dye aggregates

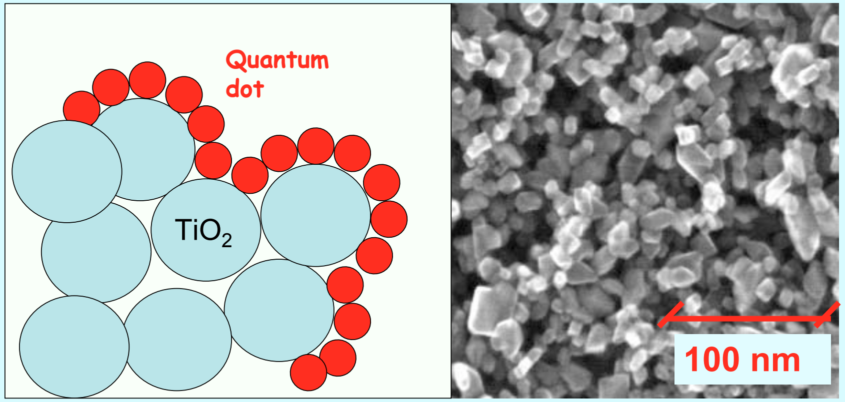




Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- redox active ionic liquids
- tandem devices

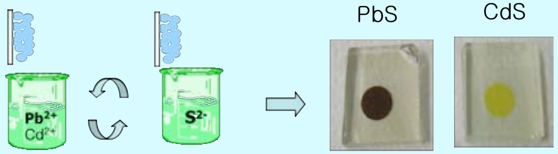
Quantum dot sensitizers for mesoscopic solar cells

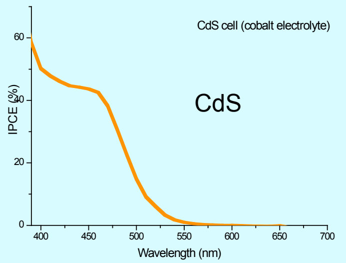


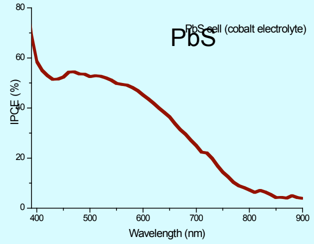
The electrons ad holes move in different phases and are separated by a phase boundary

Quantum dot sensitizers reach 60 percent IPCE

Direct deposition of PbS by CBD method







Data : Dr. Hy-Yoong Lee

Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- redox active ionic liquids
- tandem devices

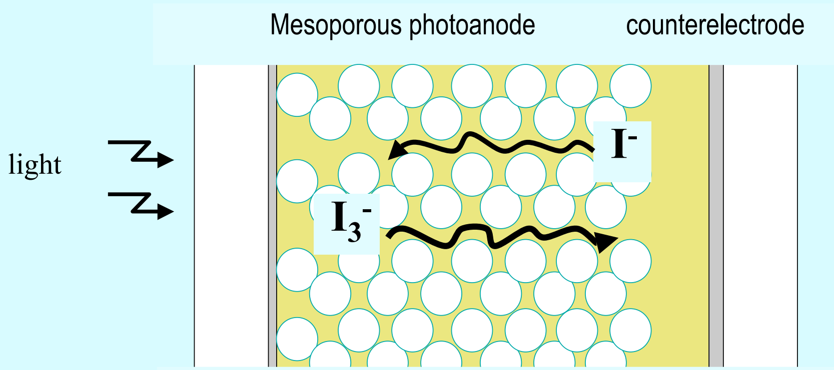
Ionic Liquids (Ils)have attractive features

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

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

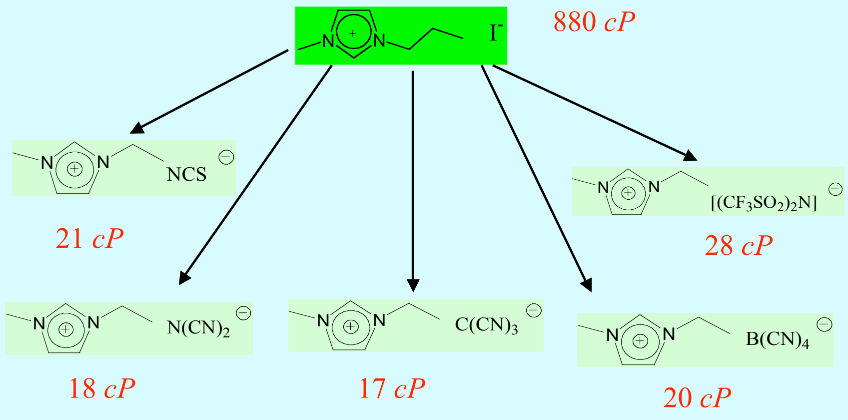
Wang, P; Zakeeruddin, S. M.; Exnar, I.; Graetzel, M..
High efficiency dye-sensitized nanocrystalline solar cells based on ionic liquid polymer gel electrolyte.
Chemical Communications (Cambridge, United Kingdom) 2002, 24, 2972-2973.

The light absorption-viscosity dilemma



Due the high viscosity of the ionic liquids, diffusion limitation of the photocurrent is expected under full sunlight.

N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, M. Grätzel, J. Electrochem. Soc. 1996, 143, 3099–3108



High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts

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

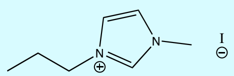
[1] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[2] Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH 1015, Lausanne, Switzerland
*These authors contributed equally to this work
†e-mail: peng.wang@ciac.jl.cn; michael.graetzel@epfl.ch

- New mixed ionic liquid (three compounds) with high conductivity
- Record conversion efficiency of 8.2%
- Excellent stability (1000h light soaking test)
- An interesting option for flexible cells

Ionic liquids

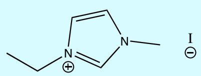
PMII

1-propyl-3-methylimidazolium iodide



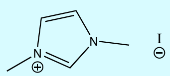
EMII

1-ethyl-3-methylimidazolium iodide



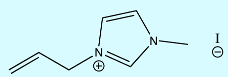
DMII

1,3-dimethylimidazolium iodide



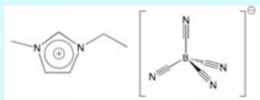
AMII

1-allyl-3-methylimidazolium iodide



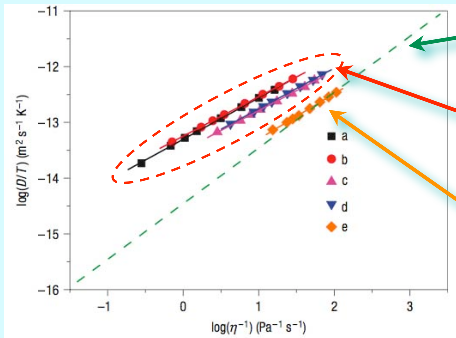
EMITCB

1-ethyl-3-methylimidazolium tetracyanoborate



Tri-iodide transport

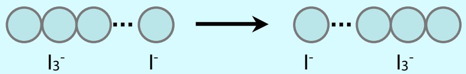
Fluidity (temp. dependent) vs. diffusion coefficient for I_3^-



Stokes-Einstein relation for hydrodynamic I_3^- radius of 2.1Å

Melts with high iodide concentration
→ Grotthus transport?

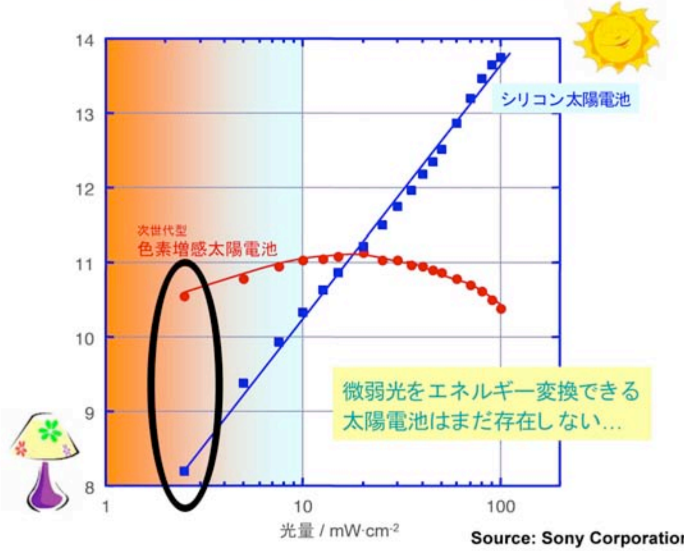
Melt with low iodide concentration



Grotthus bond exchange: enhanced diffusion coefficent

特徴 Dye sensitized solar cells outperform silicon at lower light levels

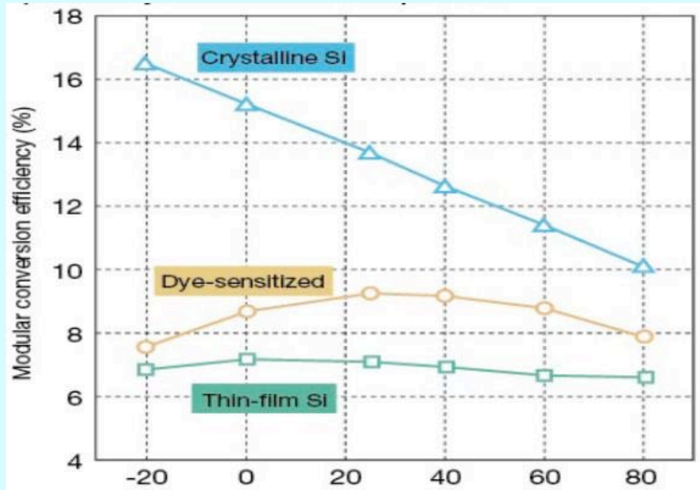
屋内希薄光エネルギーの利用



Source: Sony Corporation (2007)

Dye sensitized solar cells deliver high overall performance

Effect of temperature on module conversion efficiency



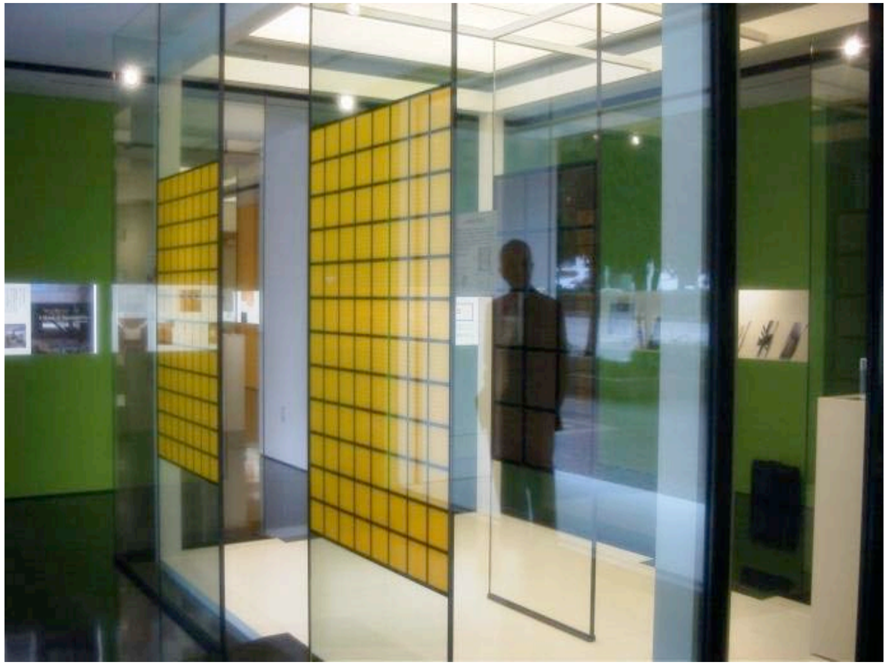
Source: *Tetsuo Nozawa*, Nikkei Electronics Asia (July 2008), Data from Sony

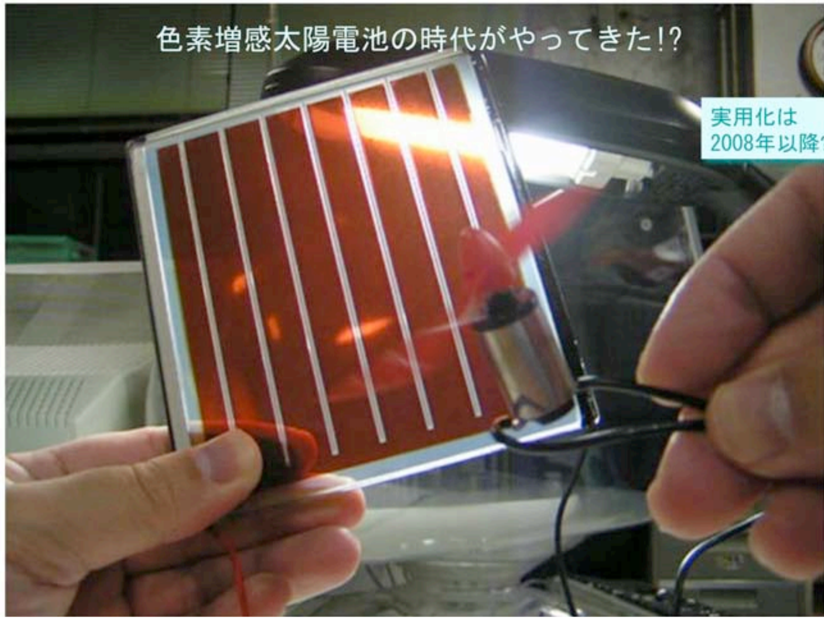
The DSC can meet future customer demands and needs

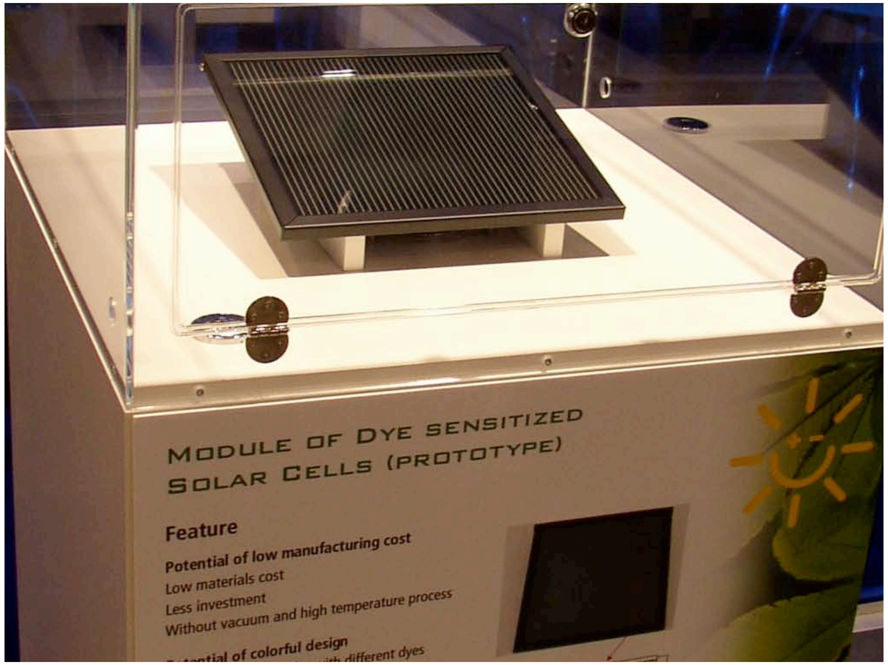
Emerging and new applications call for:

- Ease of building integration
- transparency and multicolor option (for power window application) *
- flexibility
- light weight
- Low production cost
- feedstock availability to reach terrawatt scale
- Short energy pay back time (< 1 year)
- enhanced performance under real outdoor conditions
- Bifacial cells capture light from all angles
- Tandem cell configurations boost efficiency over 15 %
- Outperforms competitors for indoor applications

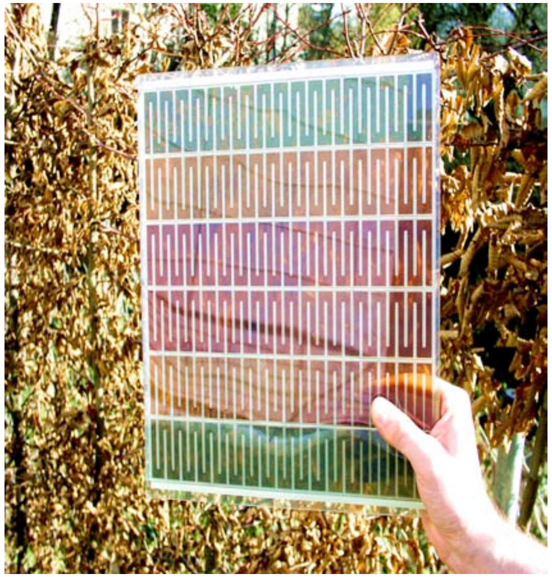
* Unique selling proposition



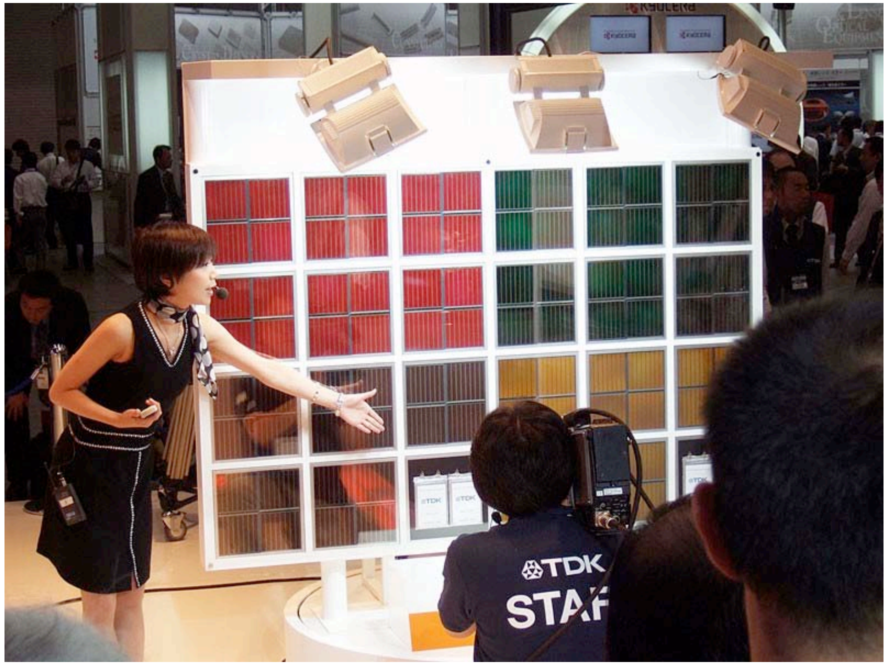




Various colours in a series-connected dye solar cell module



Courtesy Dr. Andreas Hinsch, FHI, ISE Freiburg Germany

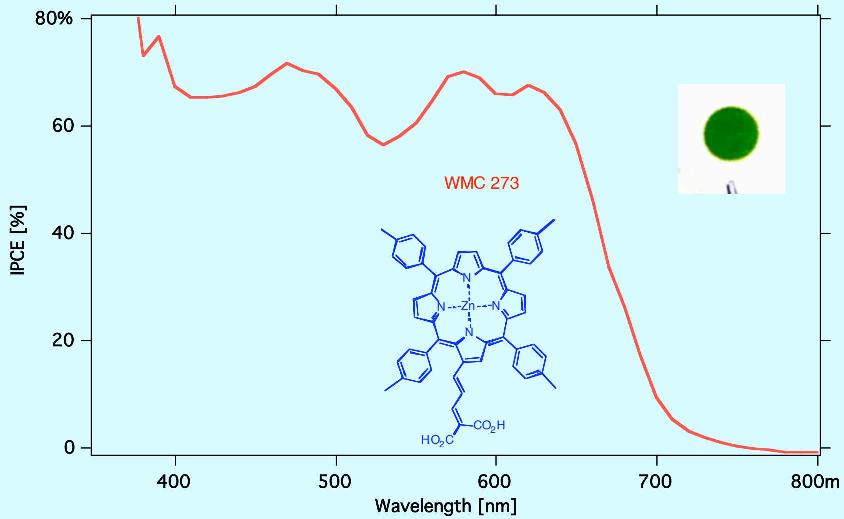


Courtesy Dr. Nam Gyu Park KIST

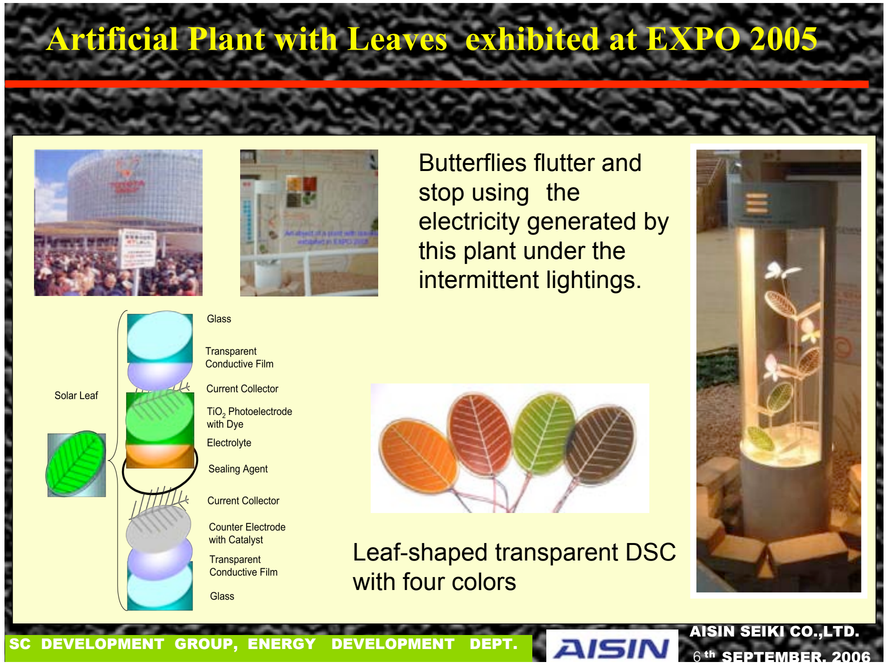
transparent, colorful, beautiful

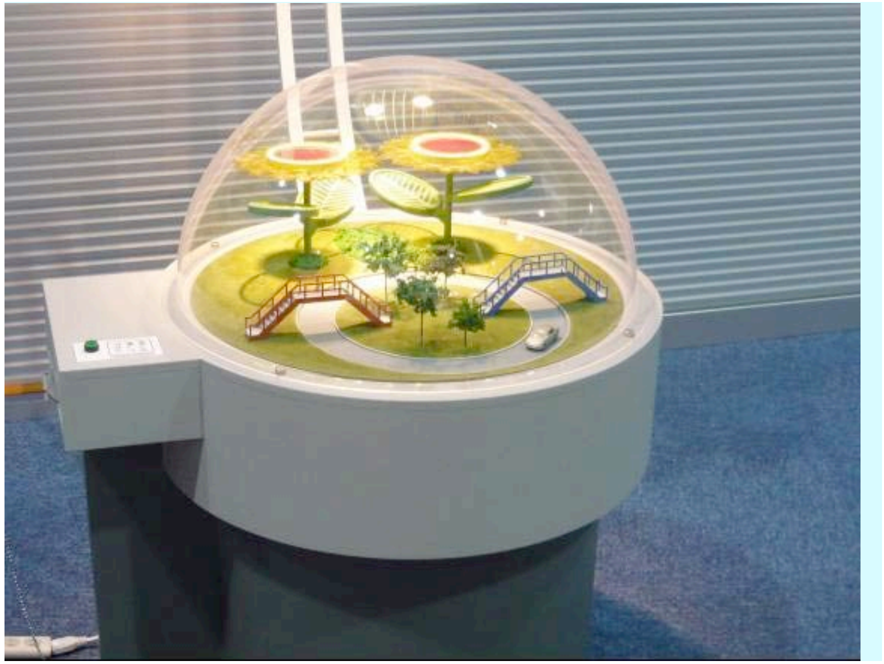
Transparency: due to nano-sized (~20 nm) TiO2 particle film
Color: due to visible light absorption by dye
* DSC costs lower than Si solar cell; 1/4 -1/5 of Si solar cell

green solar cells mimic the green leave



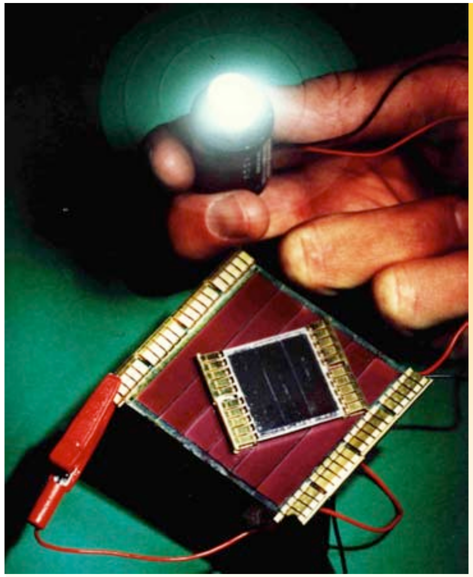
In collaboration with Professor David Officer, Univ.Wollongon,Australia

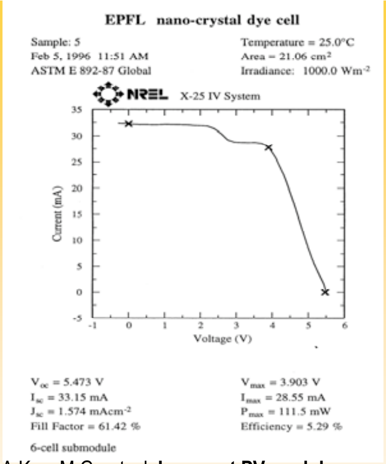




Scale-up and production

83

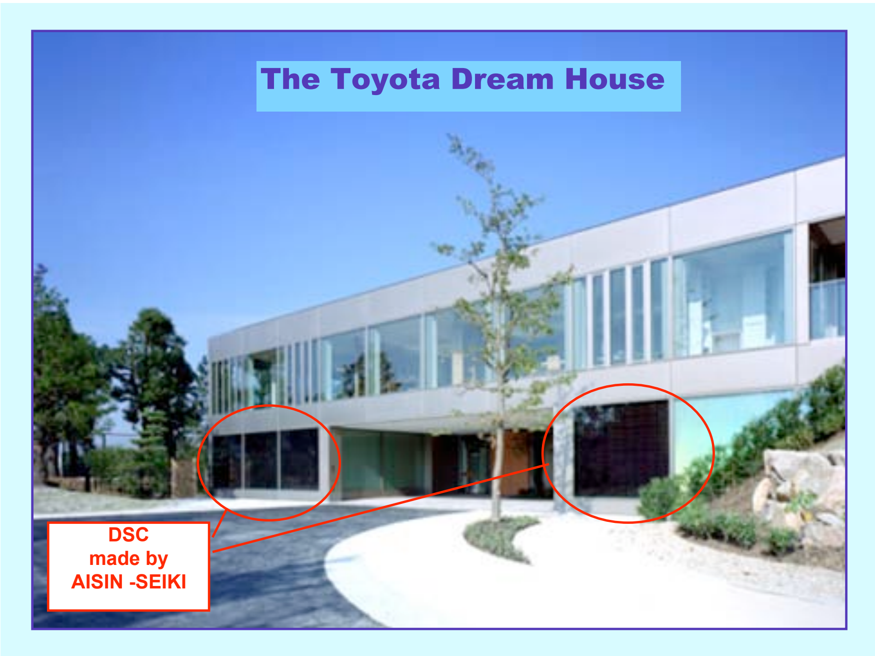


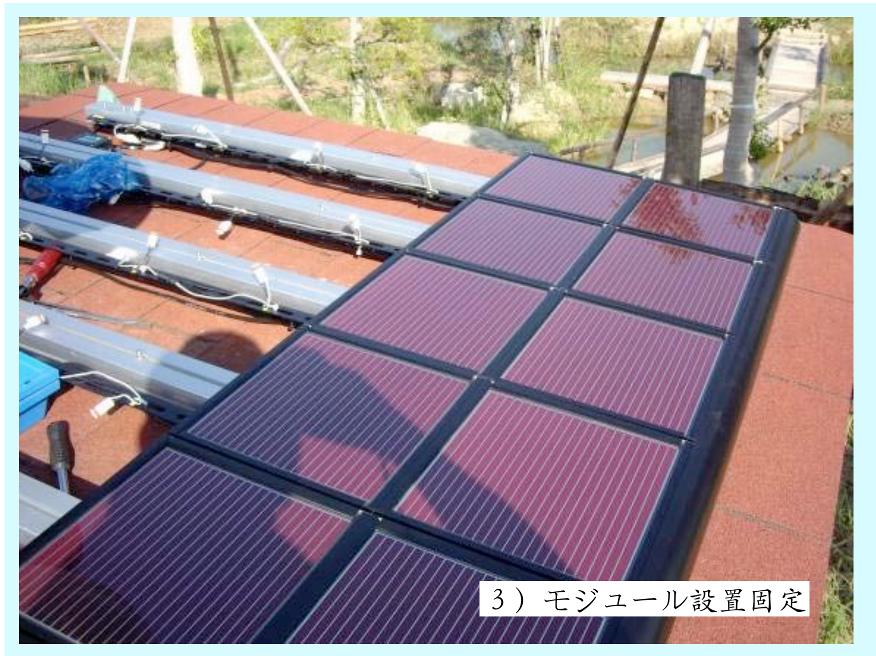


A.Kay, M.Graetzel, **Low cost PV modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder.** Solar En. Mat. Solar Cells 1996), 44(1), 99- 17.

The first monolithic in series connected DSC modules showed a validated standard AM 1.5 G conversion efficiency of 5.3 %


Real Outdoor Test of DSC Modules
Module Unit
Outdoor Test
Series connected
64 DSC cells
Kariya City at lat. 35°10'N,
Asimuthal angle: 0°
Facing due south, Tilted at 30°


The Toyota Dream House
DSC
made by
AISIN -SEIKI


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

yddion News

Tuesday, 17th October 2

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.

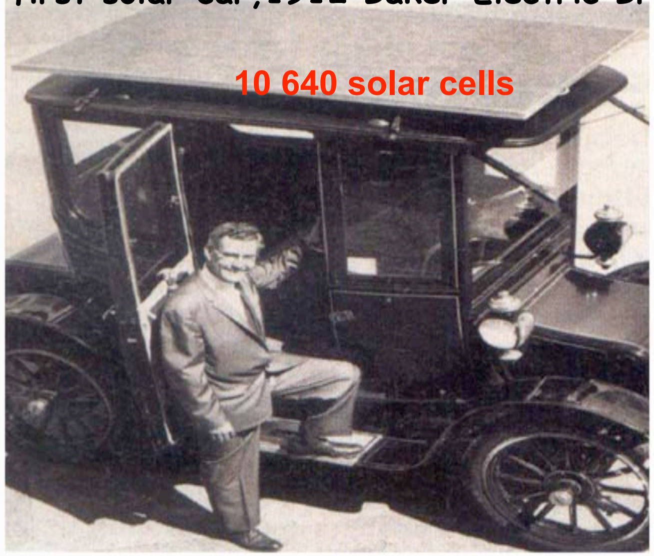
The company also believes there is an opportunity to integrate the cells in building products that can meet part of a building's energy requirements and further reduce carbon emissions.

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

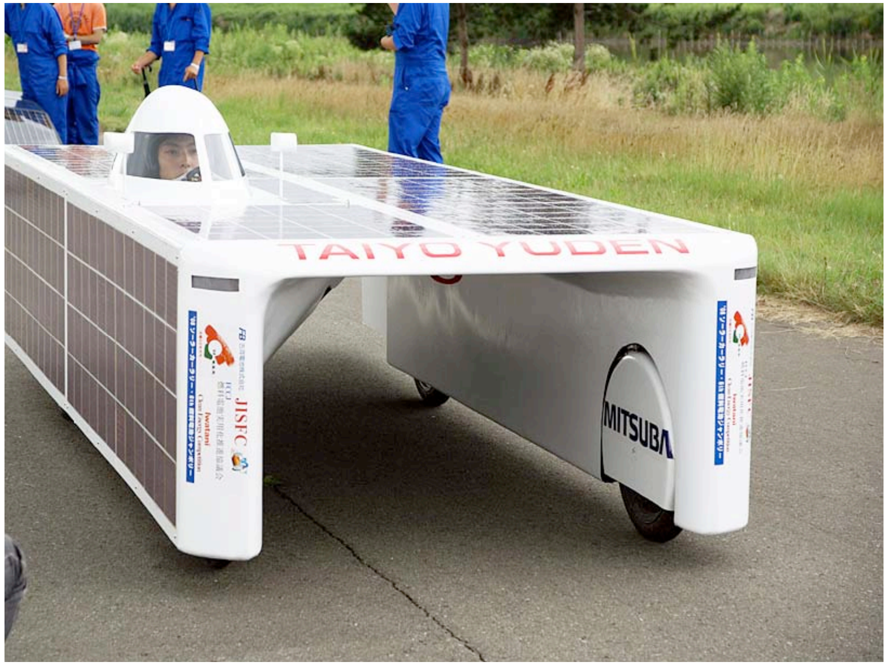
World first solar car, 1912 Baker Electric Brougham



Electric car: Tesla Roadster

AC induction motor, 200 kW, 35 kg,
6831 Li-cells 18650 (Ø 18 x 65 mm), 50 kWh, 450 kg
range 400 km per charge, acceleration to 100 km/h in 4 s
price $ 92.000

http://www.teslamotors.com



The First Solar Car Driven by DSSC

Professor Uchida: http://kuroppe.tagen.tohoku.ac.jp/~dsc