

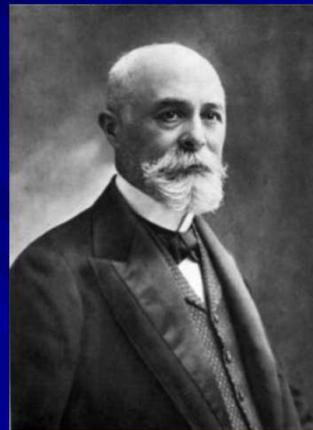
“CELDAS FOTOELECTROQUIMICAS: CELDAS SOLARES DE GRÄTZEL”

Enrique A. Dalchiele

Instituto de Física, Facultad de Ingeniería, Montevideo, URUGUAY

Historical background

- Edmond Becquerel (March 24, 1820 - May 11, 1891).
- The experiment investigated the effect of light on conductive plates - platinum and gold, on which there was only a weak thermoelectric effect; brass, which showed some photocorrosion, and finally the strong photovoltaic effect with silver halides (Cl, Br, I).



His study was considered the first paper on **photoelectrochemistry**.

COMPTRE RENDU
DES SÉANCES
DE L'ACADÉMIE DES SCIENCES.

SÉANCE DU MARDI 30 JUILLET 1859.

PRÉSIDENTE DE M. CHEVREUL.

MÉMOIRES ET COMMUNICATIONS

ÉLECTRO-CHIMIE. — *Recherches sur les effets de la radiation chimique de la lumière solaire, au moyen des courants électriques; par M. EDMOND BECQUEREL.* (Extrait par l'auteur.)

« On a étudié jusqu'ici les radiations particulières émanées d'un faisceau lumineux qui réagissent sur les éléments des corps pour opérer leur combinaison ou leur séparation, seulement sur un petit nombre de substances comme le chlorure d'argent, la résine de gaïac et quelques autres. On sait

réfraction, et même de la polarisation que les rayons lumineux dont elles font partie. Ces radiations peuvent exister dans toutes les parties du spectre, et dans chaque expérience nous nommerons radiations chimiques, celles qui affectent les substances dont nous ferons usage.

» Parmi les corps qui sont altérés par la lumière, on a remarqué que le

C. R. 1859, 2^e Semestre. (T. IX, N^o 8.)

chimie.
mie vient
décédé le

chimique de
M. EDMOND

in faisceau
leur com-
substances
es. On sait
es, rayons

LA LUMIÈRE

SES CAUSES ET SES EFFETS

PAR

M. EDMOND BECQUEREL

DE L'ACADÉMIE DES SCIENCES

DE L'UNIVERSITÉ DE FRANCE

PROFESSEUR AU GYMNASE LÉONARD DE VINCI, ETC., ETC.

TOME SECOND

EFFETS DE LA LUMIÈRE



PARIS

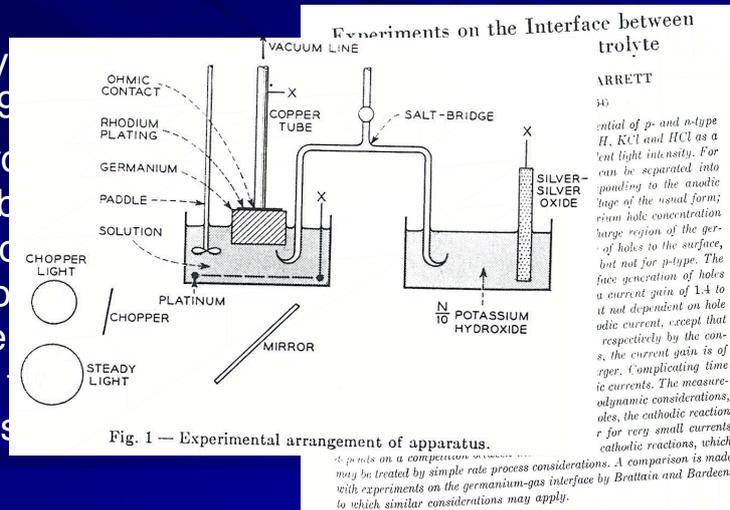
LIBRAIRIE DE FERMIN DIDOT PÈRE, FILS ET C^o

IMPRIMERIE DE L'INSTITUT, RUE JACQUIN, 66

1868

W.H. Brattain-C.G.B. Garrett

- Bell System, 1941, 1942, 1943, 1944, 1945, 1946, 1947, 1948, 1949, 1950, 1951, 1952, 1953, 1954, 1955, 1956, 1957, 1958, 1959, 1960, 1961, 1962, 1963, 1964, 1965, 1966, 1967, 1968, 1969, 1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977, 1978, 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025
- This work led to the development of the first practical semiconductor photoelectric cell and the progress of research in photoelectrochemistry.



ARRETT

34) Initial of p- and n-type Ge, KCl and HCl as a function of light intensity. For n-type Ge can be separated into anodic and cathodic regions of the usual form; for p-type Ge a large region of the generation of holes to the surface, but not for p-type. The face generation of holes a current gain of 1A to 10A is not dependent on hole recombination current, except that respectively by the concentration of holes, the current gain is of the order of 10. Complicating time constants, the cathodic reaction is very small currents, which may be treated by simple rate process considerations. A comparison is made with experiments on the germanium-gas interface by Brattain and Bardeen, to which similar considerations may apply.

Interest in photoelectrochemistry of semiconductor blossomed after...

- V.A. Myamlin, Yu V. Pleskov, "Electrochemistry of Semiconductors", Plenum Press, New York, 1967.
- H. Gerisher in *Semiconductor Electrochemistry*: in Physical Chemistry: An advanced treatise (Eds.: H. Eyring, D. Henderson, W. Jost), 9A, Academic Press, New York, 1970, p. 463.

Chronological order in which the monocrystalline semiconductors were studied

n-Ge	1955
n-Si	1958
n-CdS	1960
n-, p-GaAs	1965
n-ZnO	1966
p-NiO	1966
n-ZeSe	1967
n-, p-GaP	1968
n-SnO ₂	1968
n-KTaO ₃	1968

Kenichi Honda, 1972

Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of

It is possible that the hydrogen evolution reaction shifts towards more positive potential than normal when suitable p-type semiconductor electrodes are irradiated, in the same way that photosensitized oxygen evolution occurs with n-type semiconductor electrodes. If such a p-type semiconductor electrode is used instead of the platinum electrode, electrochemical photolysis of water may occur more effectively.

AKIRA FUJISHIMA

Department of Applied Chemistry,
Kanagawa University, Yokohama

KENICHI HONDA

Institute of Industrial Science,
University of Tokyo, Roppongi, Tokyo

Received September 13, 1971; final revision April 24, 1972.

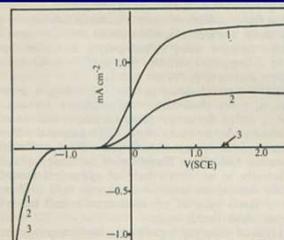


Fig. 1. Current-voltage curves for TiO₂ n-type semiconductor. A single crystal wafer of n-type TiO₂ (rutile) was used after

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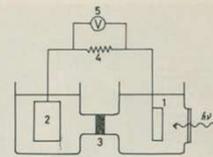
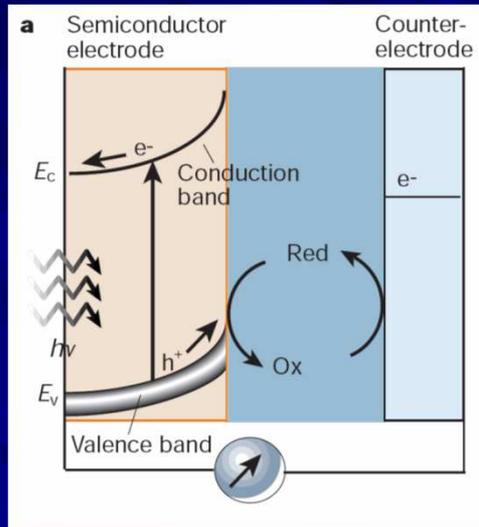
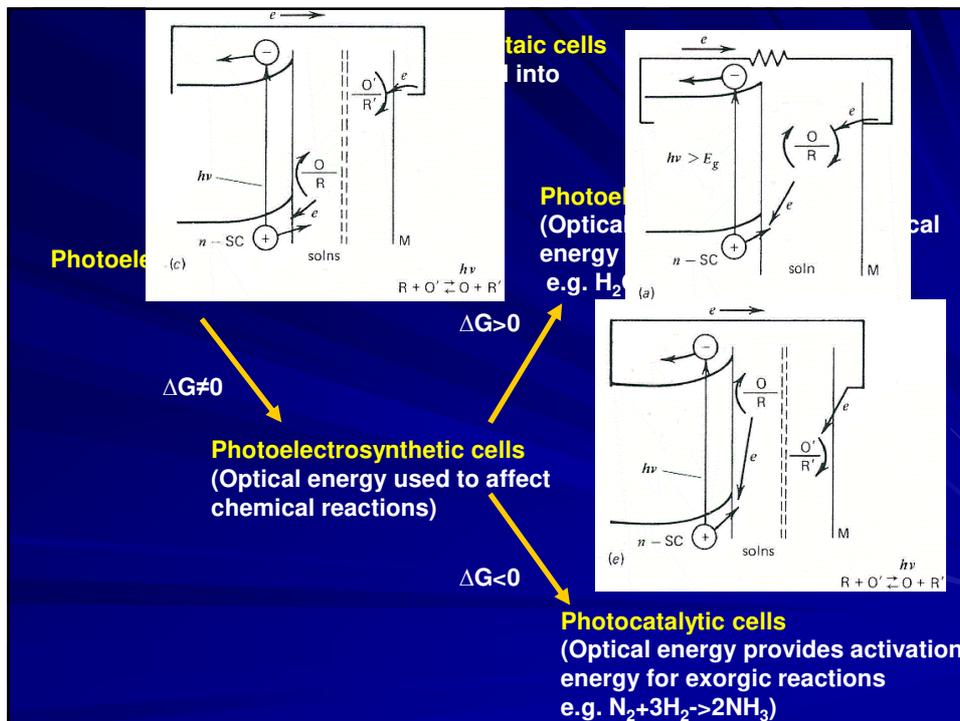


Fig. 2. Electrochemical cell in which the TiO₂ electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm².

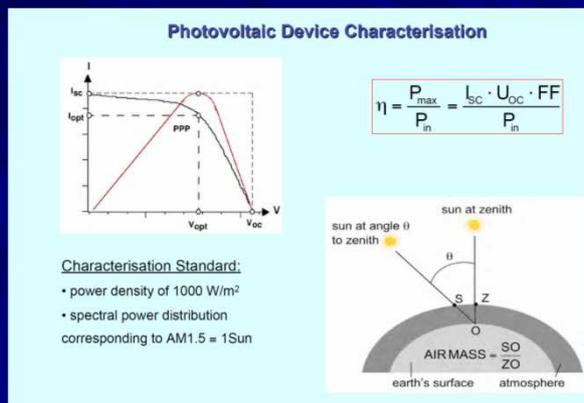
Principle of operation



Classification of PEC cells



Quantitative assessment of the solar cell performance



η : overall white light-to-electrical conversion efficiency

Table I. Other parameters to evaluate solar cell performance.

Parameters	Representation	Significance
Incident light intensity	$I_L^{25,26}$	The relationship between this parameter and short circuit current (I_{sc}) is often used to correlate how many photons contribute to electron generation and to assess carrier recombination and charge-transfer kinetics losses.
Open-circuit potential	V_{oc}^{25}	This parameter is a measure of how efficient the charge separation is in a given semiconductor-liquid combination.
Power	$P = I_{sc} * V_{oc}^{27}$	It is an estimate of how much power can be drawn from the solar cell. P_{max} is the maximum power output.
Fill factor	$P_{max}/V_{oc} * I_{sc}^{27}$	It is a lumped parameter that indicates how well the system is operating. This estimate includes contributions such as the light absorption efficiency and the number of electrons generated and transported across the film.

IPCE: incident photon-to-current conversion efficiency for monochromatic radiation

$$\text{Quantum yield } (\phi) = \frac{\text{number of charge carriers } (n)}{\text{number of photons } (N)}$$

multiply and divide by e/s to estimate current per unit area

$$(\phi) = \frac{\frac{en/s}{eN/s} = \frac{I_{sc}(\text{amp/cm}^2)}{eN/s/\text{cm}^2}}{\quad} \quad (i)$$

Total incident power (P) in watt/cm² is given as

$$P = Nh\nu = Nh \frac{c}{\lambda}$$

$$N = \frac{P\lambda}{hc} \quad (ii)$$

substituting (ii) in (i)

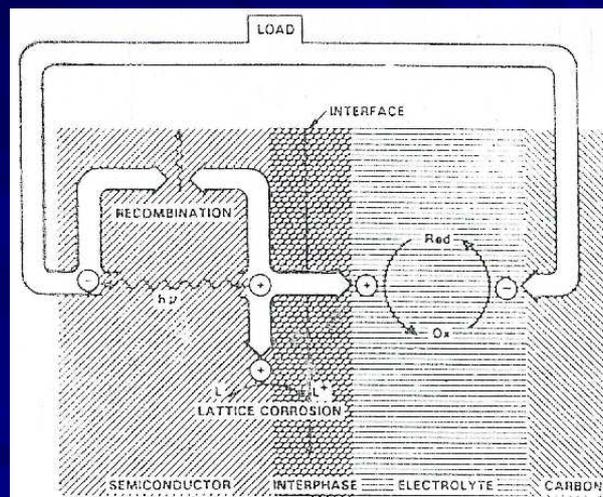
$$(\phi) = \frac{I_{sc}hc}{eP\lambda} = \frac{I_{sc}(\text{amp/cm}^2) \times 6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m/s}}{1.6 \times 10^{-19} \text{ coulombs} \times P(\text{watt/cm}^2) \times \lambda(\text{nm}) \times 10^{-9} \text{ m}}$$

$$\text{IPCE}(\phi)\% = \frac{1240 \times I_{sc}(\text{amp/cm}^2)}{P(\text{watt/cm}^2) \times \lambda(\text{nm})}$$

An ideal photoanode should...

- absorb light from a substantial part of the solar spectrum efficiently,
- offer high surface area (to absorb maximum light),
- effectively utilize the absorbed energy to produce maximum electron-hole pairs,
- facilitate rapid transport of the charges,
- be inexpensive and easily available,
- be non-corrosive and non-toxic, and
- be stable in the electrolyte for a long time.

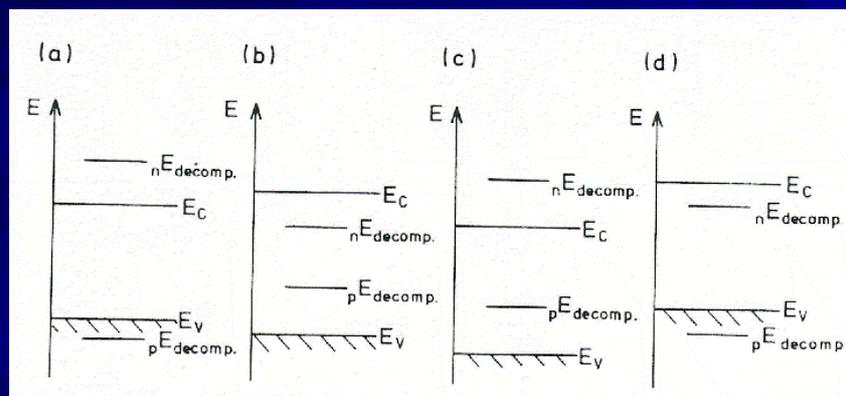
Photocorrosion



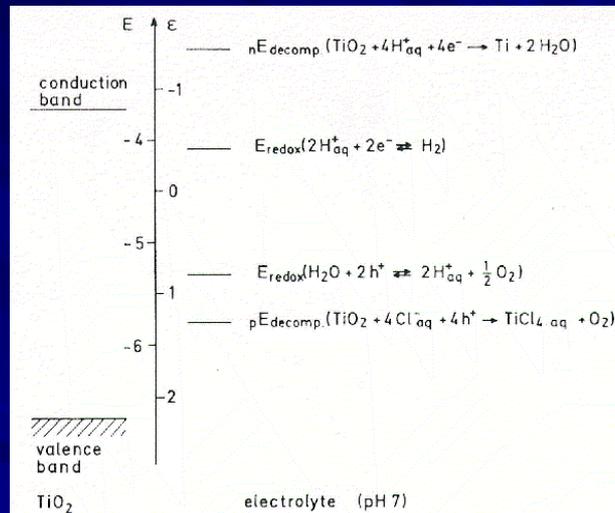
Photocorrosion

- Narrow bandgap semiconductors whose photo-response matches the solar spectrum are in general unstable in contact with electrolytes: **PHOTOCORROSION!!!**
- The width of the band gap is a measure of the chemical bond strength. Semiconductors stable under illumination, typically oxides of metals such as titanium or niobium, therefore have a wide band gap, an absorption edge towards the ultraviolet and consequently an insensitivity to the visible spectrum.
- The resolution of this dilemma: separation of the optical absorption and charge-generating functions.

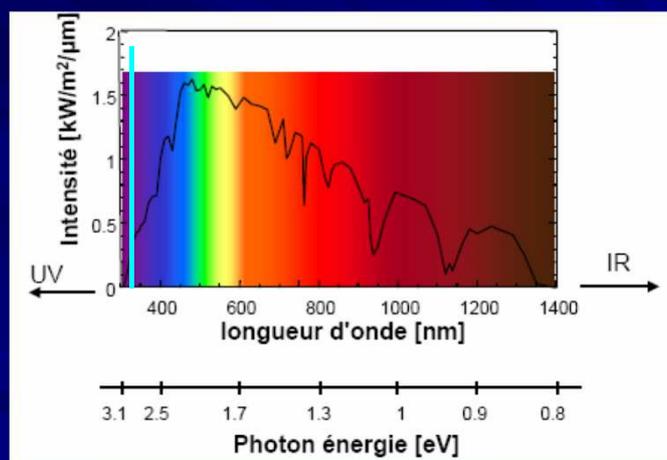
Gerisher diagrams



Gerisher diagram for TiO₂



Extension of the photoresponse of TiO₂ into the visible range



Three possible ways to extend the photoresponse of a large bandgap semiconductor

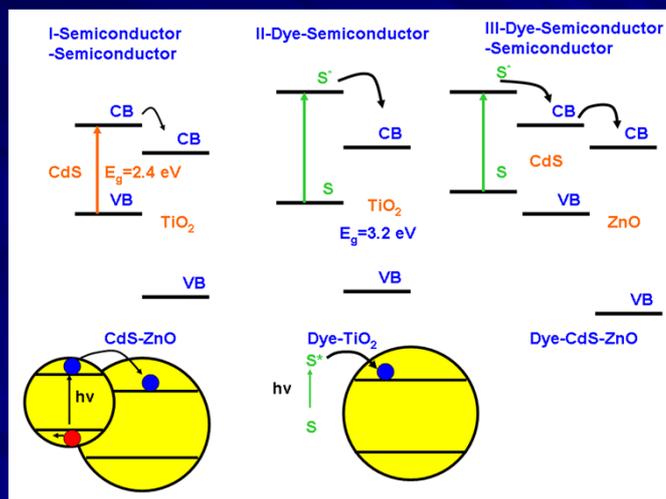
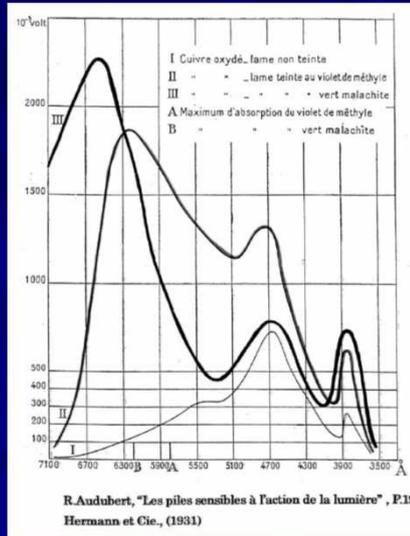


Table II. Examples of semiconductor based photoanode composites.

Composite materials	Example	IPCE	Application	Ref.
Semiconductor and metal	TiO ₂ -Au TiO ₂ -Pt	5% 28% 27%	Minimize charge recombination, improve photocurrent.	18
Semiconductor and dye	TiO ₂ -Ru based dye	60% 80%	Dye improves the ability of the photoanode to absorb light from visible and IR regions.	30
Semiconductor with another semiconductor	TiO ₂ -CdSe	5% 16%	Depending upon the particle size of the CdSe component, different sections of visible light can be absorbed.	31
Doped semiconductor and dye	TiO ₂ -N-doped TiO ₂ -Ru-CBB ^a	28% 14% 28%	While the TiO ₂ alone is not photoactive in the visible, the addition of dye to the doped TiO ₂ makes it photoactive in the visible.	32

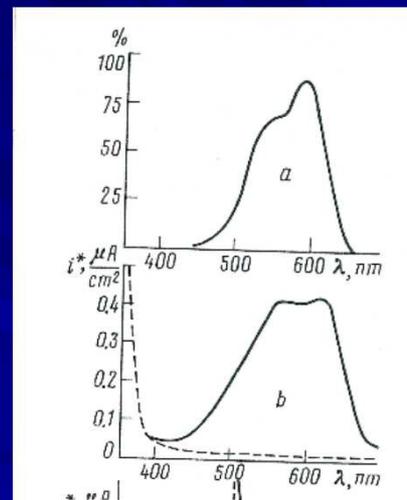
^a Ru-CBB: cisdithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium (II)

R. Audubert, 1931



Gerisher, 1977

■ ZnO/ crystal violet



Michael Grätzel, 1991

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ 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 methods¹. 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%)

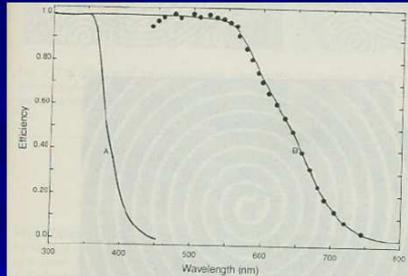
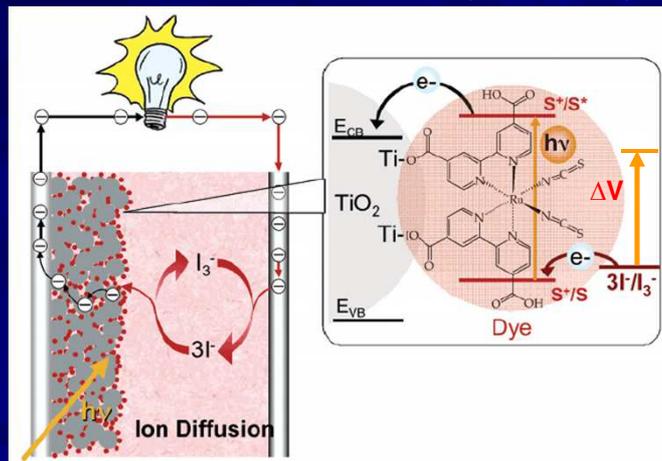


FIG. 3 Absorption and photocurrent action spectra of TiO₂ films supported on conducting glass. A, absorption efficiency of the bare TiO₂ film corrected for conducting glass background; B, absorption efficiency of the same film coated with a monolayer of **1**, full circles, monochromatic current yield at short circuit as a function of excitation wavelength. Yield is corrected for 15% loss of incident photons through light absorption and scattering by the conducting glass support.

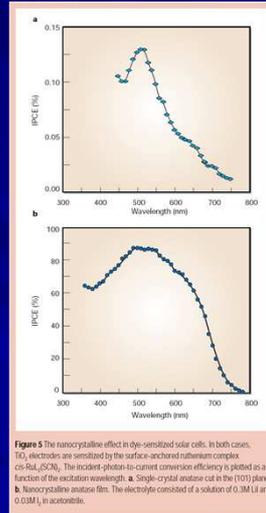
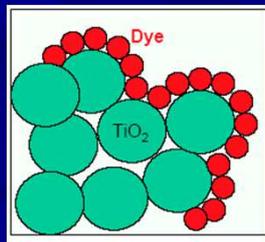
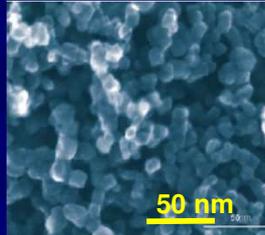
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Operating Principles of the Dye-Sensitized Solar Cell (DSSC)

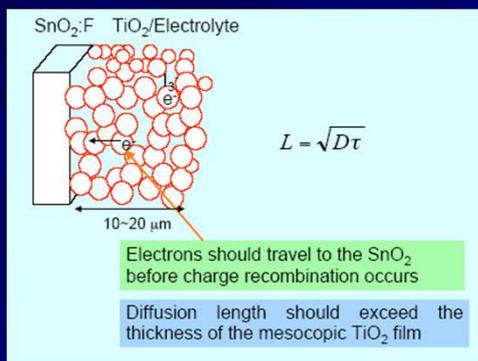


TiO₂ + Dye

Nanocrystalline morphology of TiO₂ film enhances light harvesting by surface adsorbed dye monolayer.



A Key Parameter: the electron diffusion length



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

$D = 10^{-4} \text{ cm}^2/\text{s}$, $\tau = 1 \text{ s}$, $L = 100 \text{ μm}$

Photoinduced Electron Transfer Mechanism

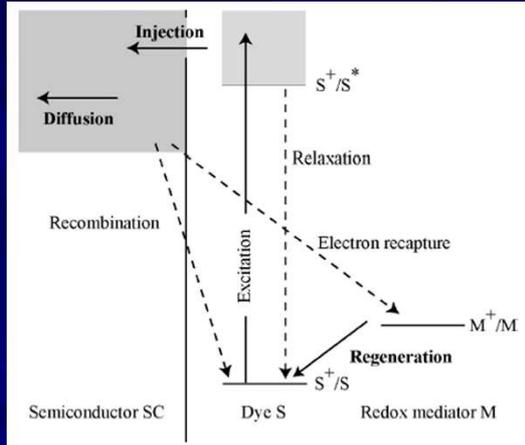
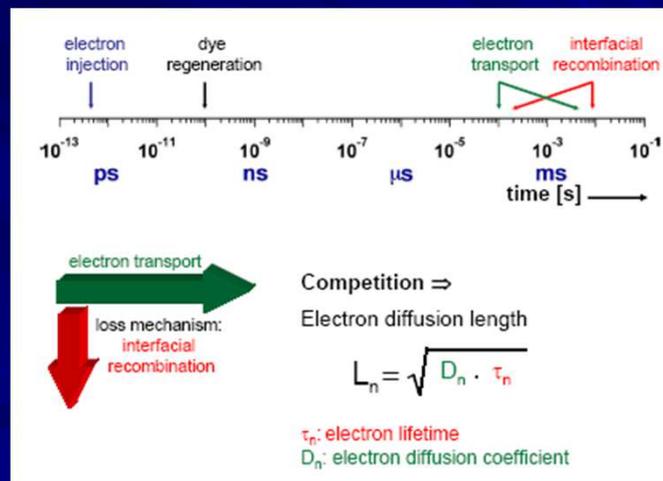


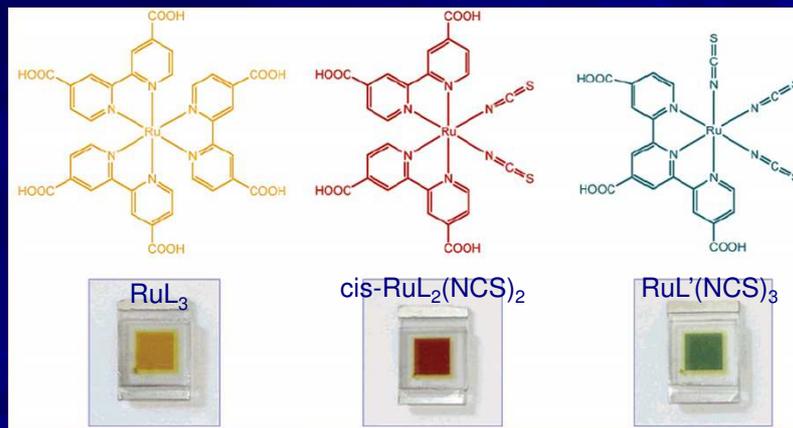
Table 2. Orders of magnitude for the different electron transfer processes rates taking place in a classical DSSC.

Process	Time frame
Excitation	Femtosecond
Injection	Femtosecond
Relaxation	Picosecond
Recombination	Micro-millisecond
Regeneration of dye	Nanosecond
Electron recapture reaction	Micro-millisecond

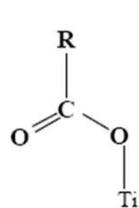
Dynamic Competition



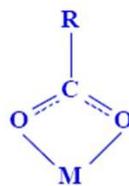
Ruthenium sensitizers



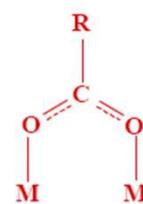
Possible anchoring modes of carboxylate group on TiO₂ surface



Unidentate



Chelating



Bridging bidentate

However with this sensitizer, the HOMO-LUMO gap is about 2.0 eV, and as a result the photovoltaic response is limited above wavelengths of 600 nm., as shown in Fig.3 (curve RuL₃; L = dicarboxylbipyridyl, or dc bpy). With detailed molecular engineering, the electronic structure of the molecule was modified to raise the HOMO level and thereby extend the response towards the red end of the spectrum. Fig. 3 presents this progress, first using cyanide (CN) and later thiocyanide (SCN) substituents. Ultimately a "black dye", absorbing across the whole visible spectrum and providing a panchromatic response, was evolved by associating the ruthenium "core" with a terpyridyl complex, and three spectrum-modifying thiocyanide groups

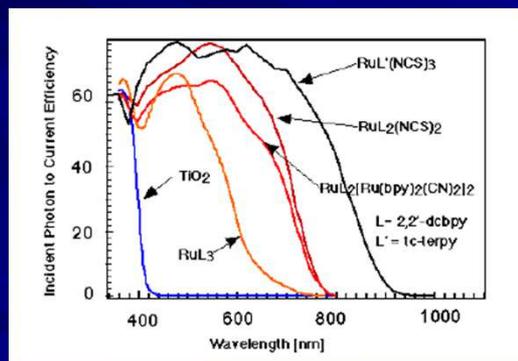


TABLE 1: Record efficiencies of DSC of various device sizes.

Dye*	Surface area (cm ²)	η (%)	V _{oc} (V)	I _{sc} (mA/cm ²)	FF (%)	Reference
N-719	<1 cm ²	11.2	0.84	17.73	74	[8]
N-749	0.219	11.1	0.736	20.9	72	[9]
N-749	1.004	10.4	0.72	21.8	65	[10]
N-719	1.31	10.1	0.82	17.0	72	[11]
N-3	2.36	8.2	0.726	15.8	71	[12]
N-749	26.5 (submodule)	6.3	6.145	1.7	60	[13]

* N-719, N-749, and N-3 are codes for molecular structures (see Section 5.1).

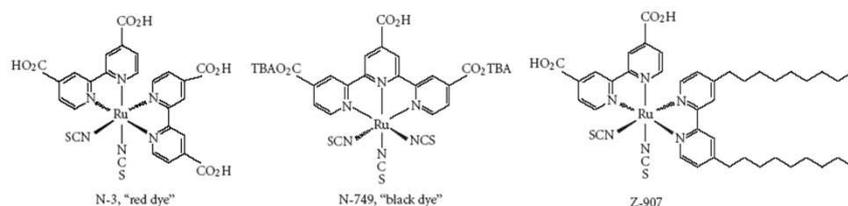
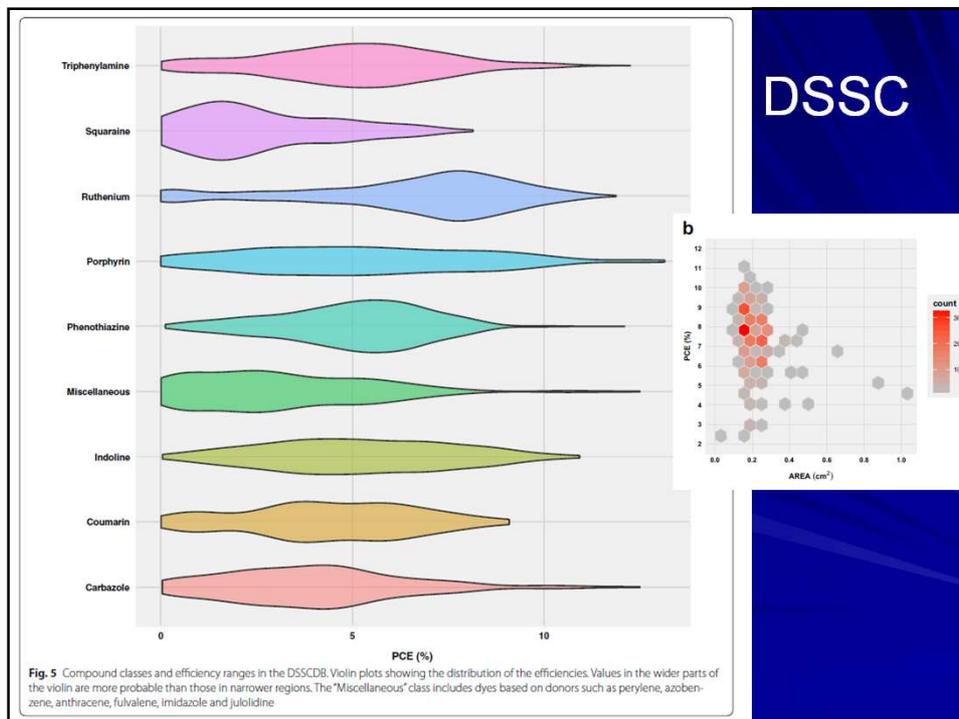


FIGURE 2: The three most frequently applied ruthenium polypyridyl complexes.



IPCE: incident photon-to-current conversion efficiency for monochromatic radiation

- It is a measure of the effectiveness in converting photons incident on the cell to photocurrent flowing between the WE and CE.
- IPCE is also called the **external quantum efficiency**.
- IPCE is **not corrected** for losses of light by absorption in solutions, glass substrates, reflection losses at interfaces, etc..

$$IPCE = \frac{I_p(\lambda)}{eF(\lambda)}$$

$$F(\lambda) = \frac{P(\lambda)}{hc/\lambda} \quad IPCE = 1240 \left(\frac{I_p(\lambda)}{P(\lambda)\lambda} \right)$$

$$IPCE = \left(\frac{hc}{e} \right) \left(\frac{I_p(\lambda)}{P(\lambda)\lambda} \right)$$

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$$\text{Quantum yield } (\phi) = \frac{\text{number of charge carriers } (n)}{\text{number of photons } (N)}$$

multiply and divide by e/s to estimate current per unit area

$$(\phi) = \frac{en/s}{eN/s} = \frac{I_{sc}(\text{amp/cm}^2)}{eN/s/\text{cm}^2} \quad (i)$$

Total incident power (P) in watt/cm² is given as

$$P = Nh\nu = Nh \frac{c}{\lambda}$$

$$N = \frac{P\lambda}{hc} \quad (ii)$$

substituting (ii) in (i)

$$(\phi) = \frac{I_{sc}hc}{eP\lambda} = \frac{I_{sc}(\text{amp/cm}^2) \times 6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m/s}}{1.6 \times 10^{-19} \text{ coulombs} \times P(\text{watt/cm}^2) \times \lambda(\text{nm}) \times 10^{-9} \text{ m}}$$

$$IPCE(\phi)\% = \frac{1240 \times I_{sc}(\text{amp/cm}^2)}{P(\text{watt/cm}^2) \times \lambda(\text{nm})}$$

APCE: absorbed photon-to-current conversion efficiency for monochromatic radiation

- **APCE** is defined as the number of electrons (or holes) collected per absorbed photon.
- This is also called the **internal quantum efficiency**.
- It is calculated after considering the losses in the incident photons like reflection, scattering, absorption, etc..

APCE: absorbed photon-to-current conversion efficiency for monochromatic radiation

$$APCE = \frac{IPCE}{1 - 10^{-A}}$$

$$LHE = 1 - 10^{-A}$$

A=absorbance.

LHE=light harvesting efficiency or absorptance

Conversion yield of incident photons in electrical current

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

$$IPCE(\lambda) = LHE(\lambda) \phi_{\text{inj}} \eta_{\text{coll}}$$

$$APCE(\lambda) = \frac{IPCE(\lambda)}{LHE(\lambda)} = \phi_{\text{inj}} \eta_{\text{coll}}$$

■ Φ_{inj} = quantum yield of charge injection.

■ η_{coll} = efficiency of transporting injected electrons in to the external circuit.

Experimental set-up

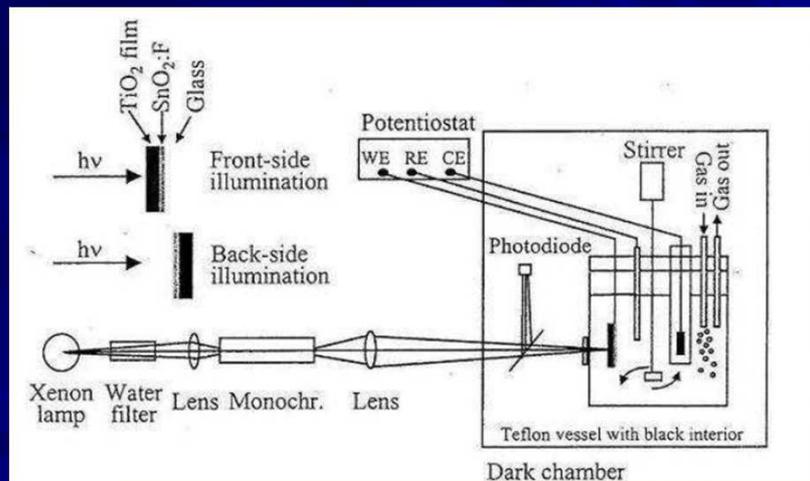
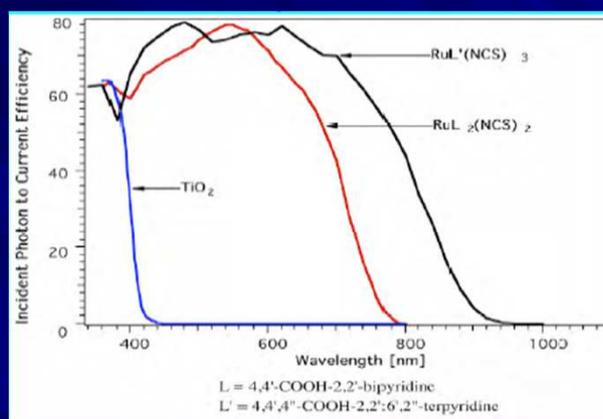


Table II. Examples of semiconductor based photoanode composites.

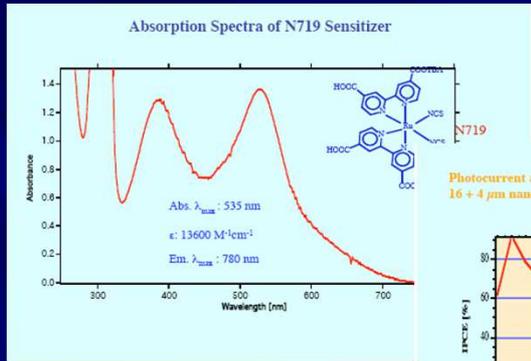
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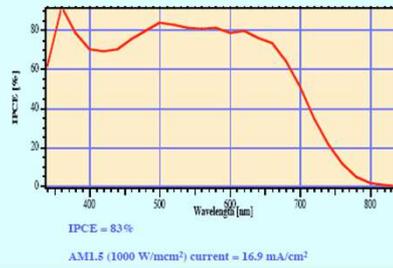
Results



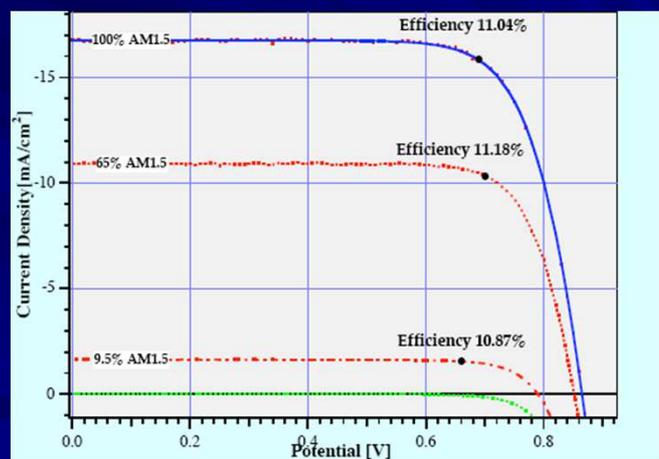
IPCE



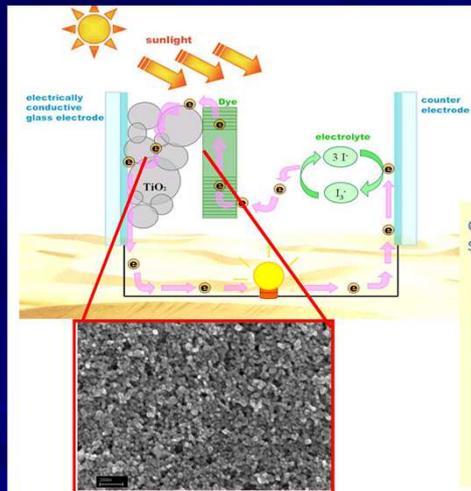
Photocurrent action spectrum obtained with the N719 dye attached to 16 + 4 μ m nanocrystalline TiO₂ film.



Overall photovoltaic performance

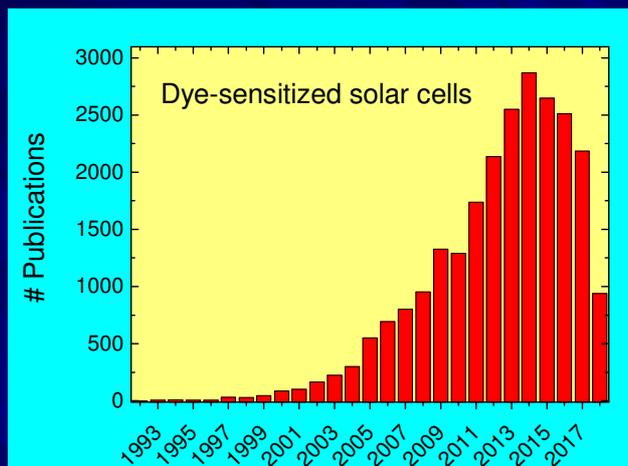


Dye Sensitized Cells Solar – DSSC

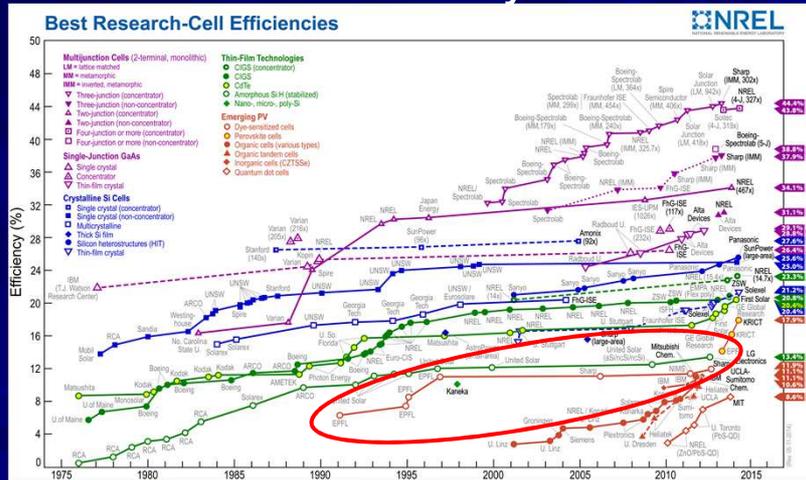


The highest demonstrated efficiency so far has been only 11 %, modules 6.3 %.

Number of Publications



Timeline of energy conversion efficiency



Stability

- **Long-term stability** is a key parameter for any type of solar cells.
- **Intrinsic factors** are related to the DSSC under the conditions of a perfectly closed/sealed system.
- **Extrinsic factors** are related to degradation processes induced by potential diffusion of molecules into or out of the solar cell (i.e.: penetration of water and oxygen and escape of solvent molecules).
- 12.000 h of continuous full intensity light exposure: no dye degradation.
- It was possible to pass the critical 1000 h accelerated thermal test at 80 °C.

DSSC Advantages vs. Silicon Solar Cells

- Low cost and ease of production
- Performance increases with temperature narrowing the efficiency gap
- Bifacial configuration - advantage for diffuse light and albedo
- Efficiency less sensitive to angle of incidence
- Transparency for power windows
- Color can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasible
- Low energy content (for silicon this is 5 GJ/m² !), payback time is only a few months as compared to years for silicon.

Road map

Parameter	Present Status (2007)	Future Goal (2015)
Champion device efficiency	11%	16%
Laboratory cell degradation	<5% after stress at 80°C for 1000 h in dark or after light-soaking for 100 h @ 1 sun at 60°C	<5% after stress at 85°C for 3000 h in the dark or after light-soaking for 3000 h @ 1 sun at 60°C
Module efficiency	5%–7%	10%
Outdoor module degradation	<15% in 4 yrs	<15% in 10 yrs
Identification of key degradation mechanisms	Degradation mechanisms are controversial	Primary degradation mechanisms identified

National Solar Technology Roadmap:

Sensitized Solar Cells

Facilitator: Rick Melton

Participants included:
National Renewable Energy Laboratory
Sandia National Laboratories
U.S. Department of Energy
University and private-industry experts

Management Report
NREL/MP-520-41739
June 2007

Commercialization

Japan

- IMRA-Aisin Seiki/Toyota
- Sharp
- Toshiba
- Dai Nippon
- Peccell Technologies

Australia

- Dyesol

USA

- Konarka

UK

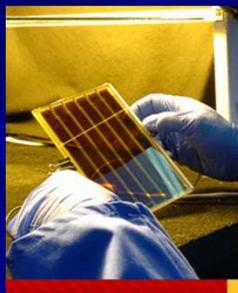
- G24i

Switzerland

- Soloronix



Outdoor installation – CSIRO (Commonwealth Scientific and Industrial Research Organization), Newcastle, Australia.



The Dyesol team established the worlds first prototype manufacturing facility for Dye Solar Cells.
Dyesol supplies equipment, materials and components for Dye Solar Cell Technology.

G24 Innovations

- G24i has announced a DSC module production of 25 MW capacity in 2007.
- With extension plans up to 200 MW by the end of 2008.
- G24i has won a grant from the World Bank to develop its technology to light homes in Rwanda (2008).

