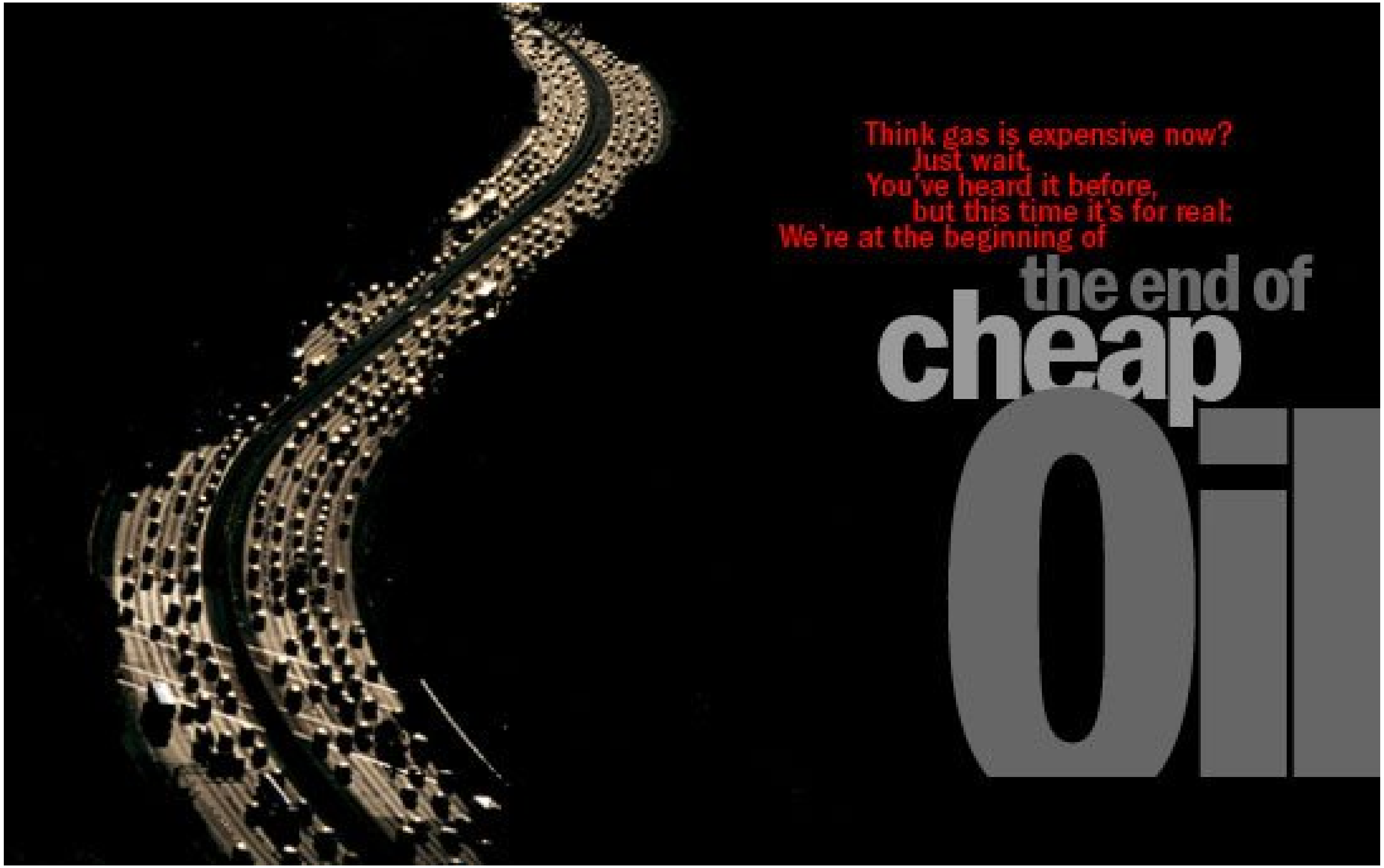
下世代太陽電池

工研院太陽光電科技中心
下世代太陽電池研究組：蔡 松 雨

2009.12.24

Background

No More Cheap Oil



National Geography, June 2004

地球暖化

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地球的污染日愈嚴重，溫室效應不退

- 1997年京都議定書於2005年2月16日生效，要求工業國家降低CO_2排放量，發展與使用再生能源，降低碳的排放是必然的趨勢
- 平均傳統能源發電之CO_2排放量530噸/GWh，太陽光電發電製造之CO_2排放量僅5噸/GWh

GWh = Giga Watt Ｘ Hour

= 10^6 kWh = 百萬度電

1 G = 1 Giga = 10^9

1 k = 1 kilo = 10^3

1 kWh = 1度電

Photo: NASA

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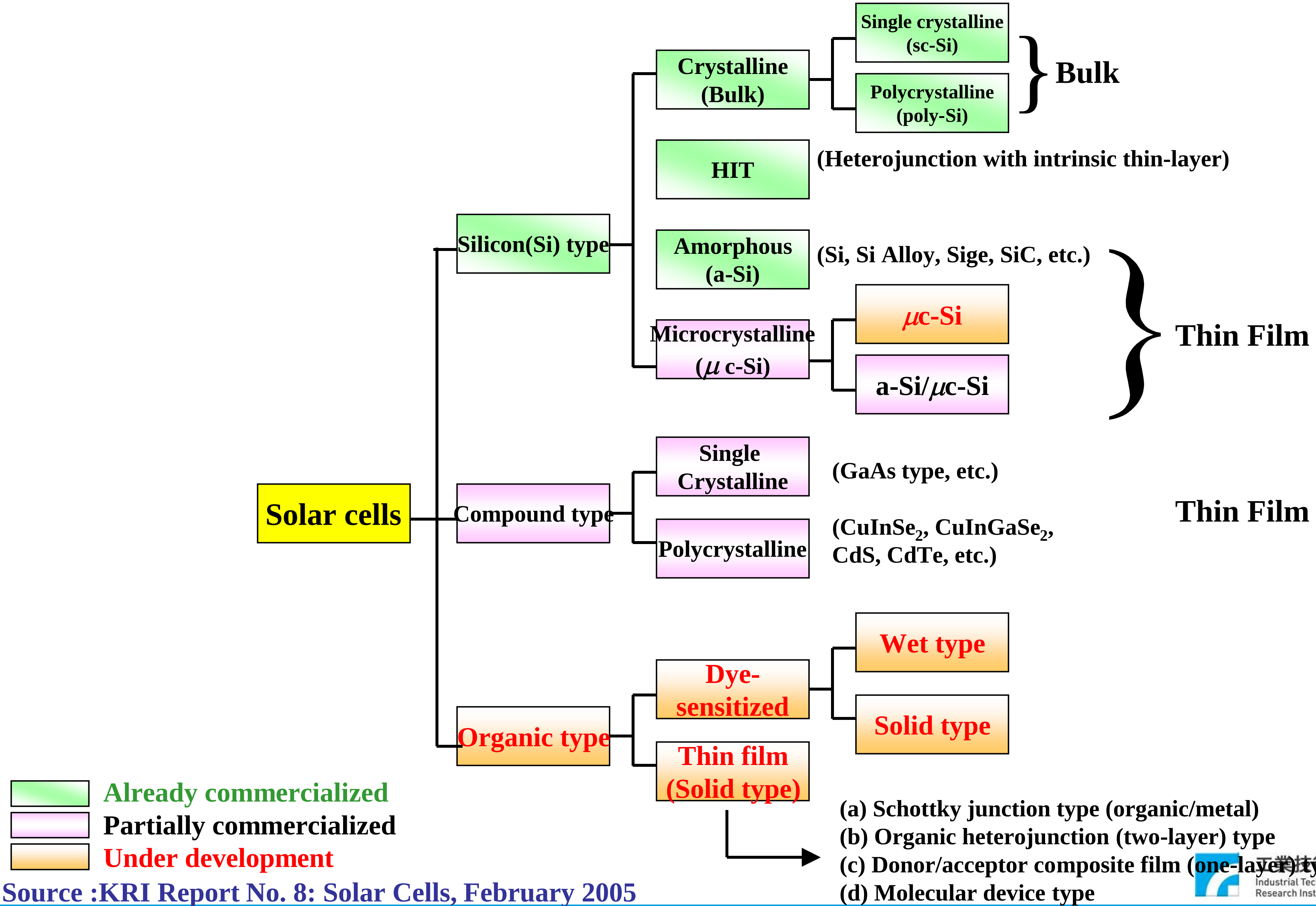
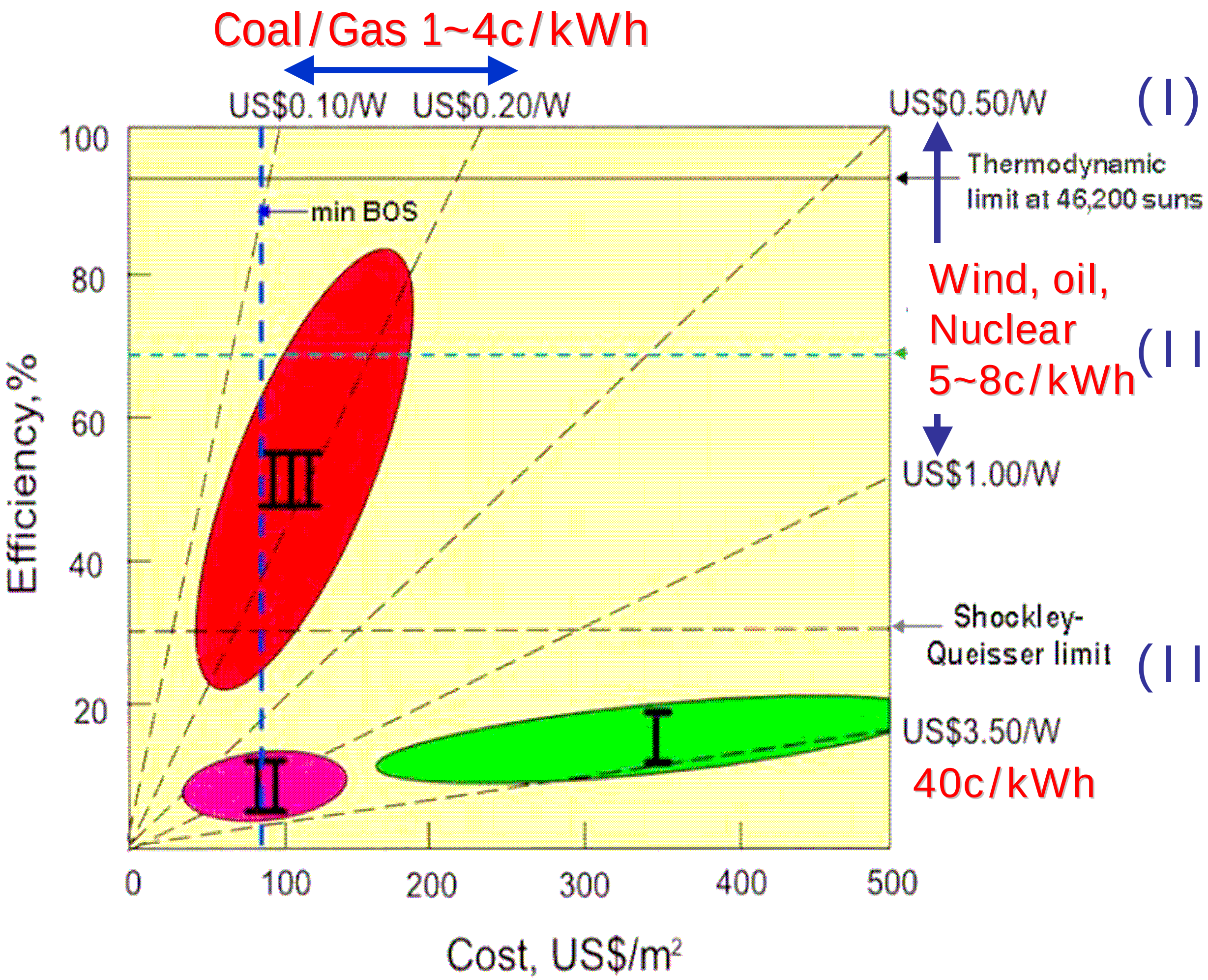
依材料劃分的太陽電池種類



Source :KRI Report No. 8: Solar Cells, February 2005

PV Generation, Cost, & Efficiency



After Martin Green

(I) c-Si solar cell
(Industry driven)

(II) Thin-film solar cell
a-Si, CdTe,
CIGS, etc..
(Innovation driven)

(III) Organic PV, DSC,
QD, CPV, etc..
(Research driven)

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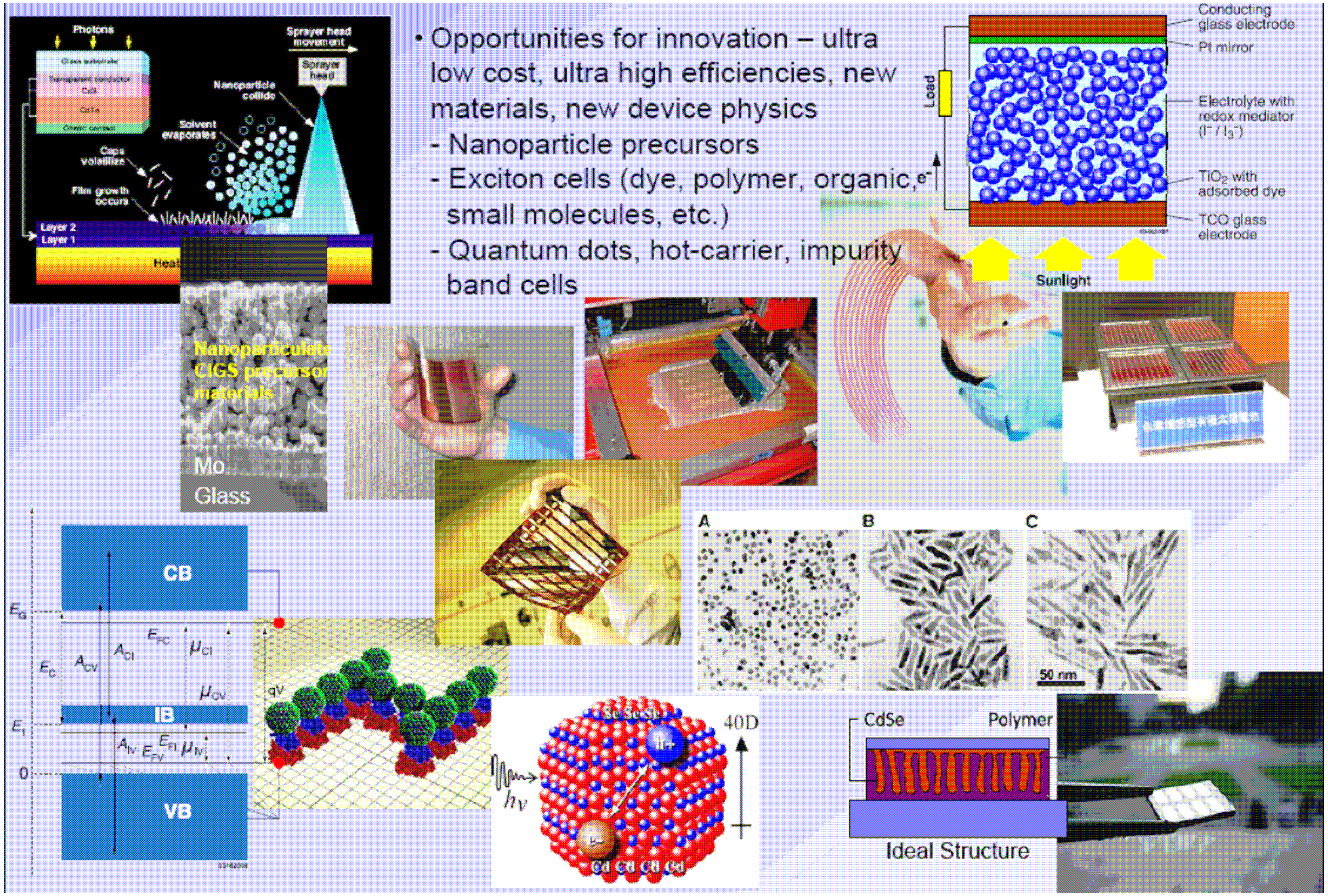
Future Generation PV Technologies

"Speed + Timing + Direction" for winning the holy grail.



Source： Thomas Surek, Solar Electricity: Progress and Challenges, 2006

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CIGS (CuInGaSe)

I-III-VI 薄膜太陽電池

I-III-VI族：$CuInSe_2$、$Cu(In,Ga)Se_2$

I	II	III	IV	V	VI
		5 B	6 C	7 N	8 O
		13 Al	14 Si	15 P	16 S
29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se
47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te

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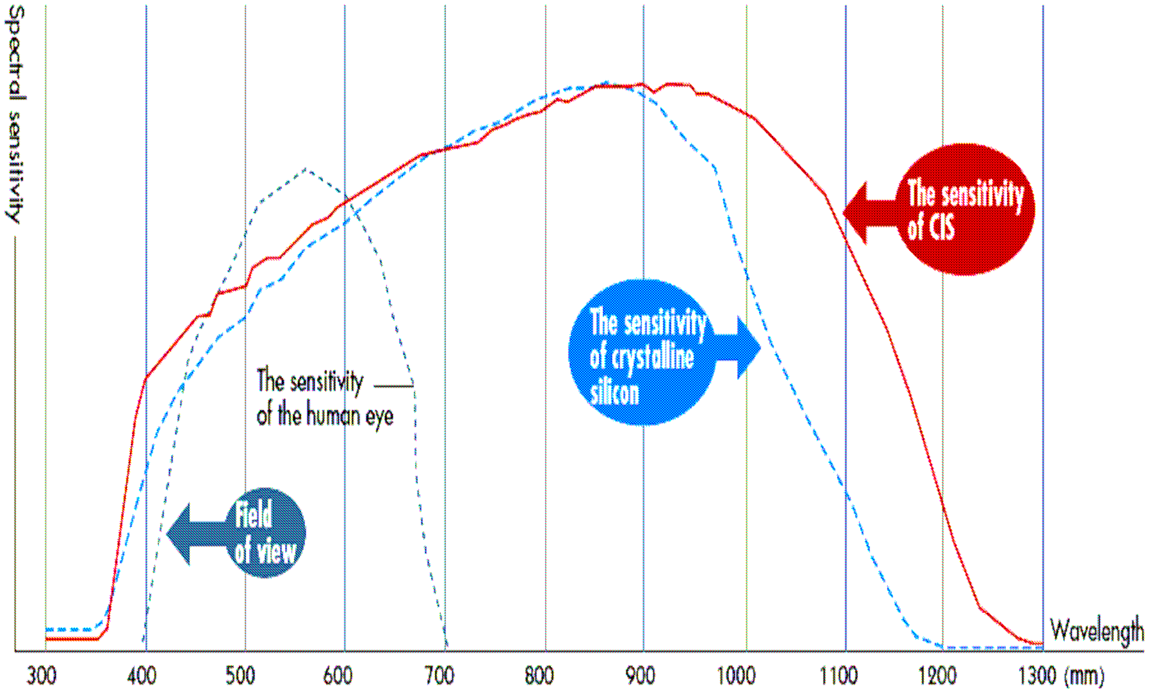
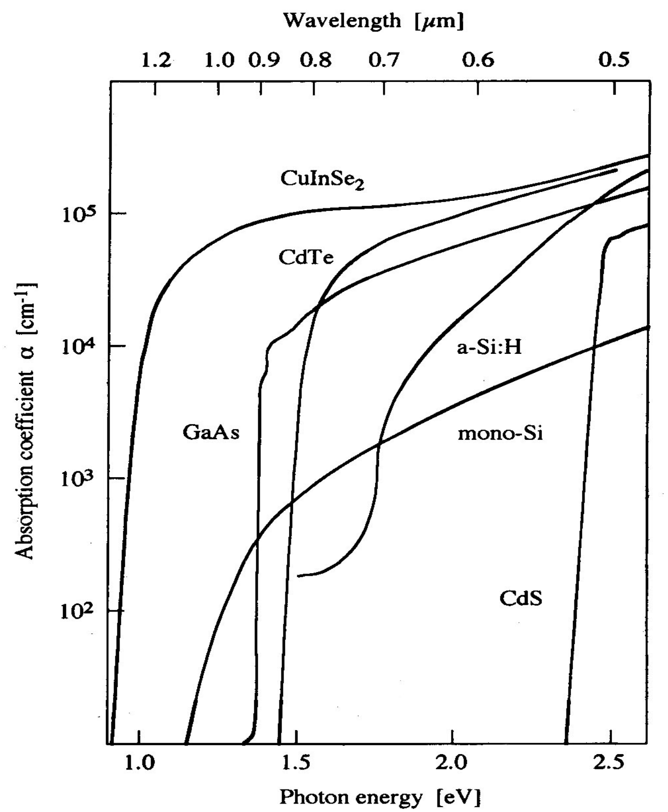
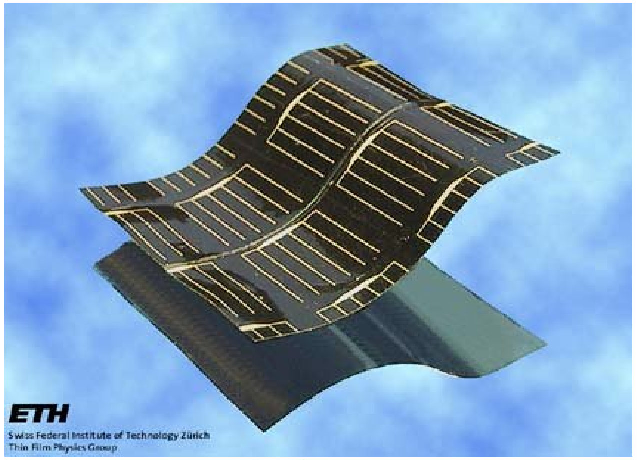
Optical superiority of CIGS

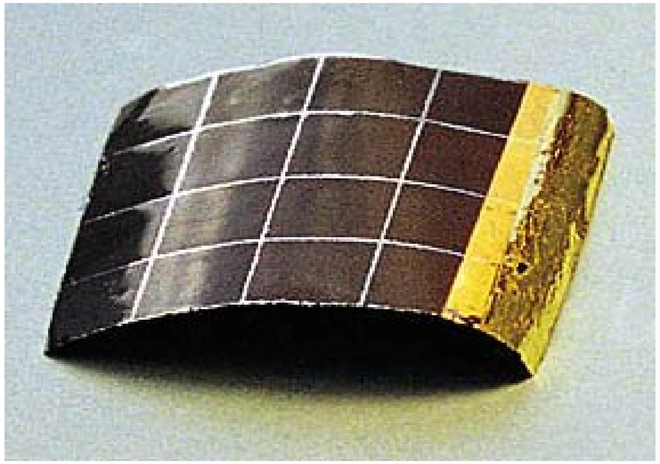
More electricity can be expected given the same environmental conditions due to its superior spectral sensitivity.

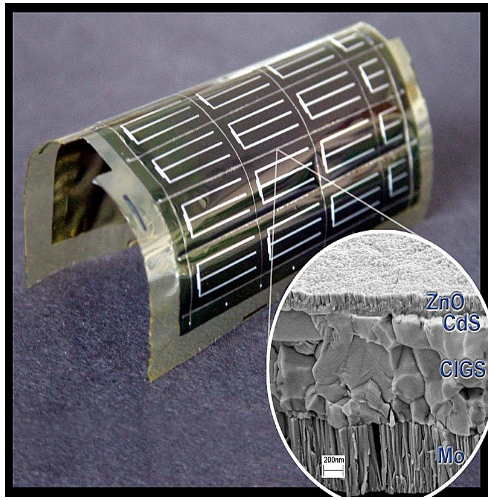


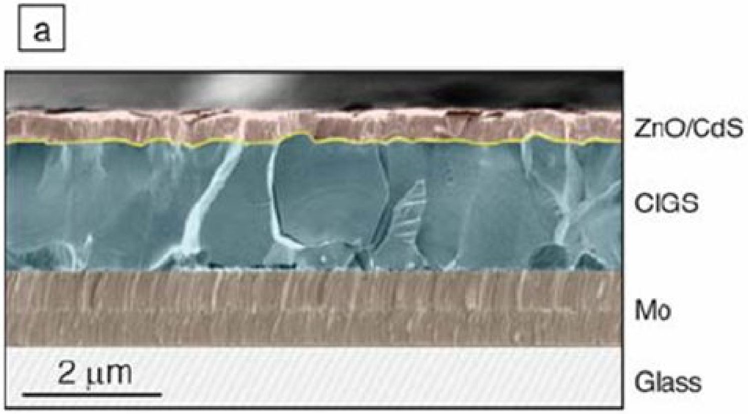


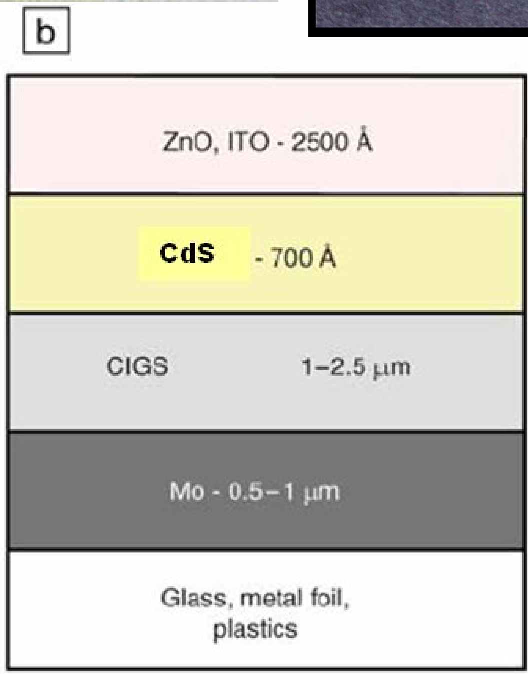
銅銦鎵硒(*CIGS*)薄膜太陽電池











Buried pn junction

Source: January 2005 *MRS Bulletin*

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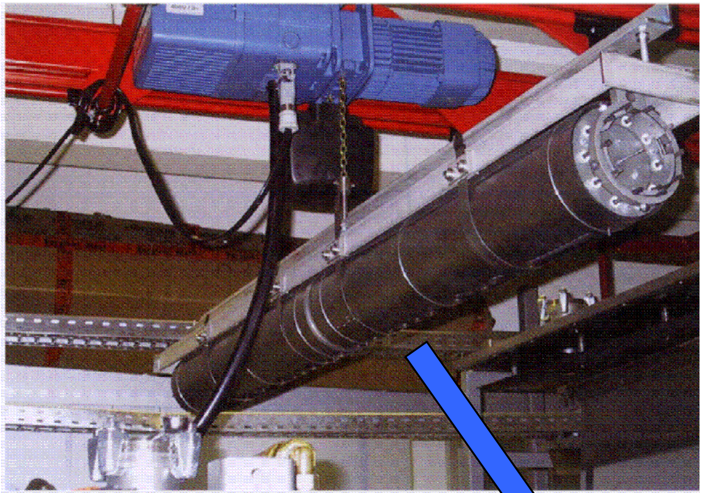
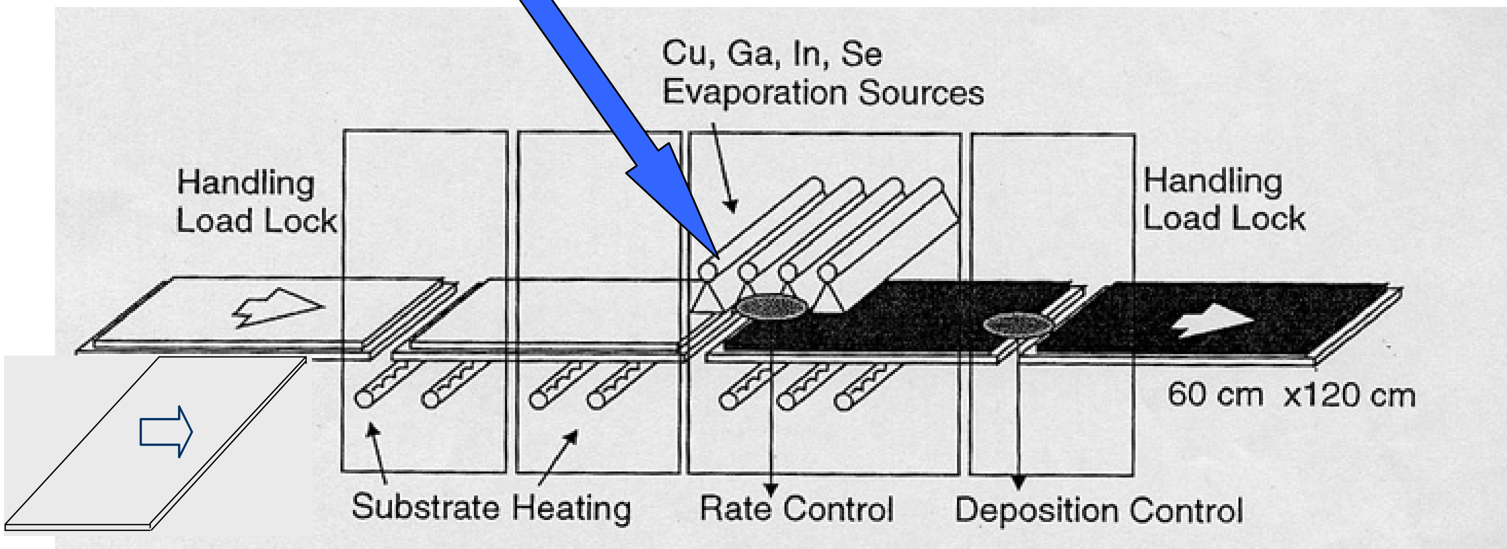
Würth Solar's CIGS Co-Evaporation





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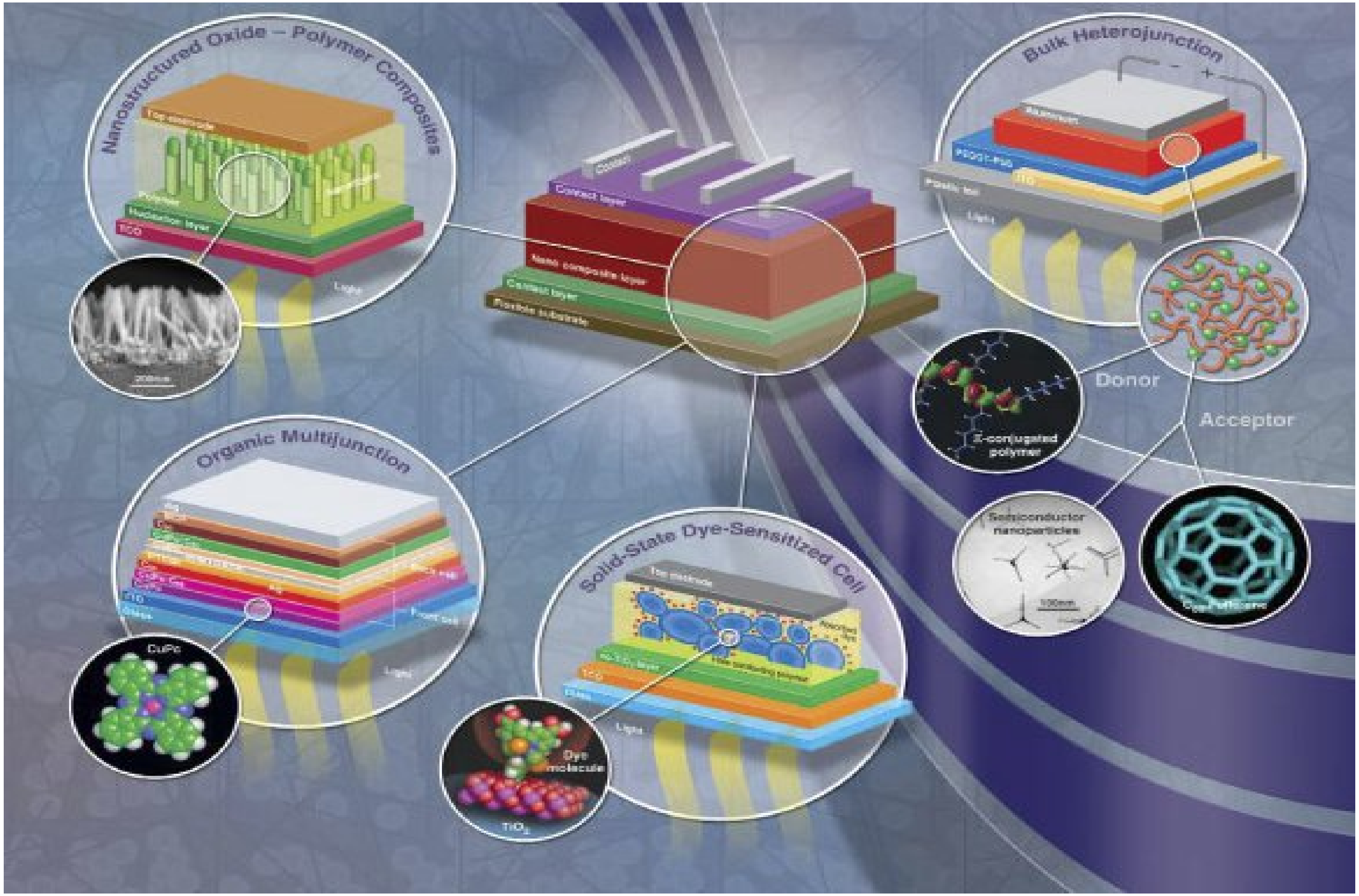
*CIGS*薄膜太陽電池

資料來源：**Global Solar Energy**

資料來源：***Professor Vivian Alberts and a team at the University of Johannesburg developed and patented a manufacturing technique to construct CIGS of 5 micron thick.***

奈米結構太陽電池



January 2005 *Materials Research Society Bulletin*

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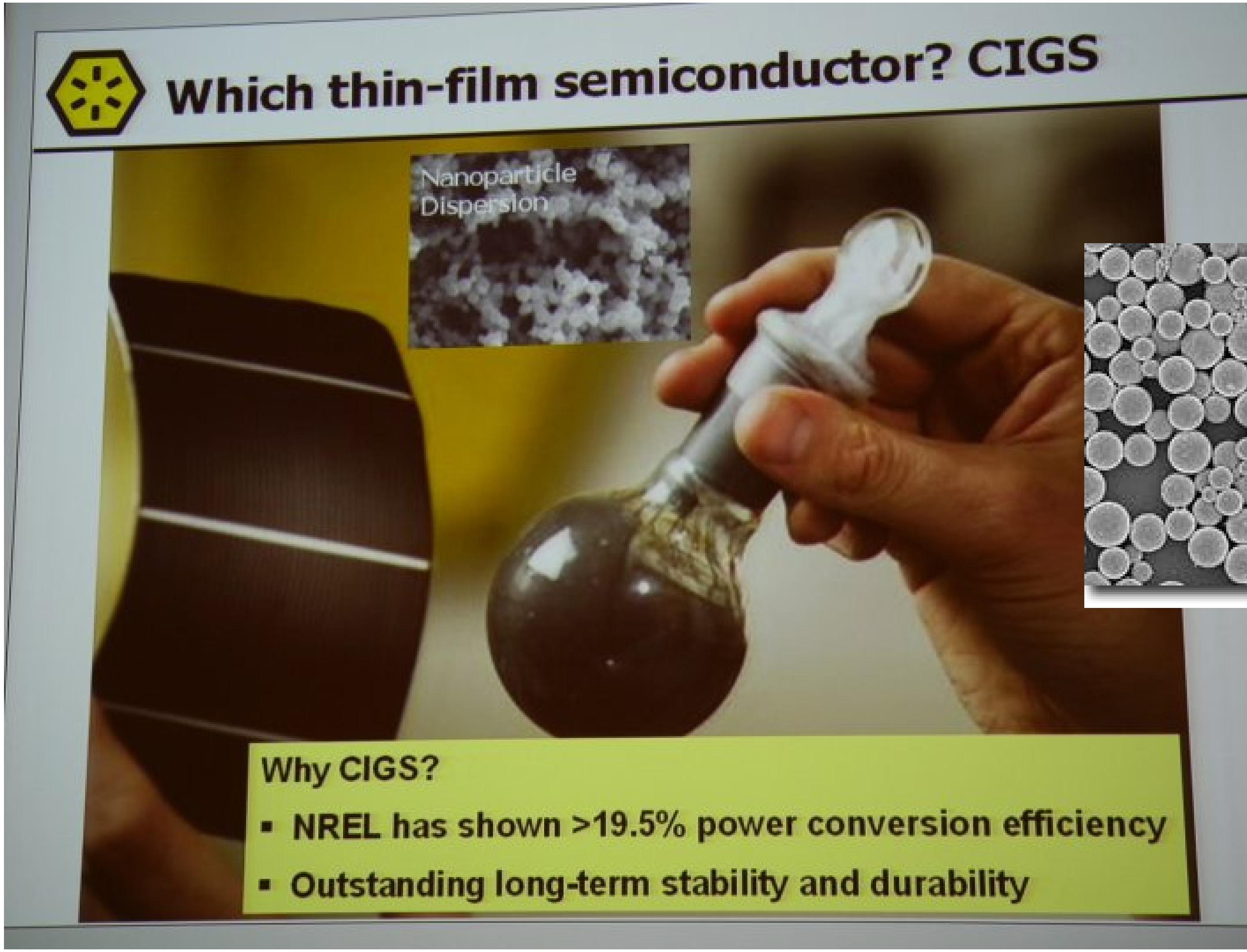
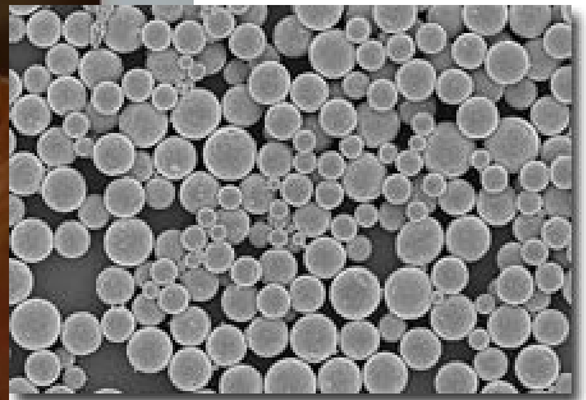
Nanosolar CIGS Ink





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CIGS: High-Vacuum vs. Non-Vacuum

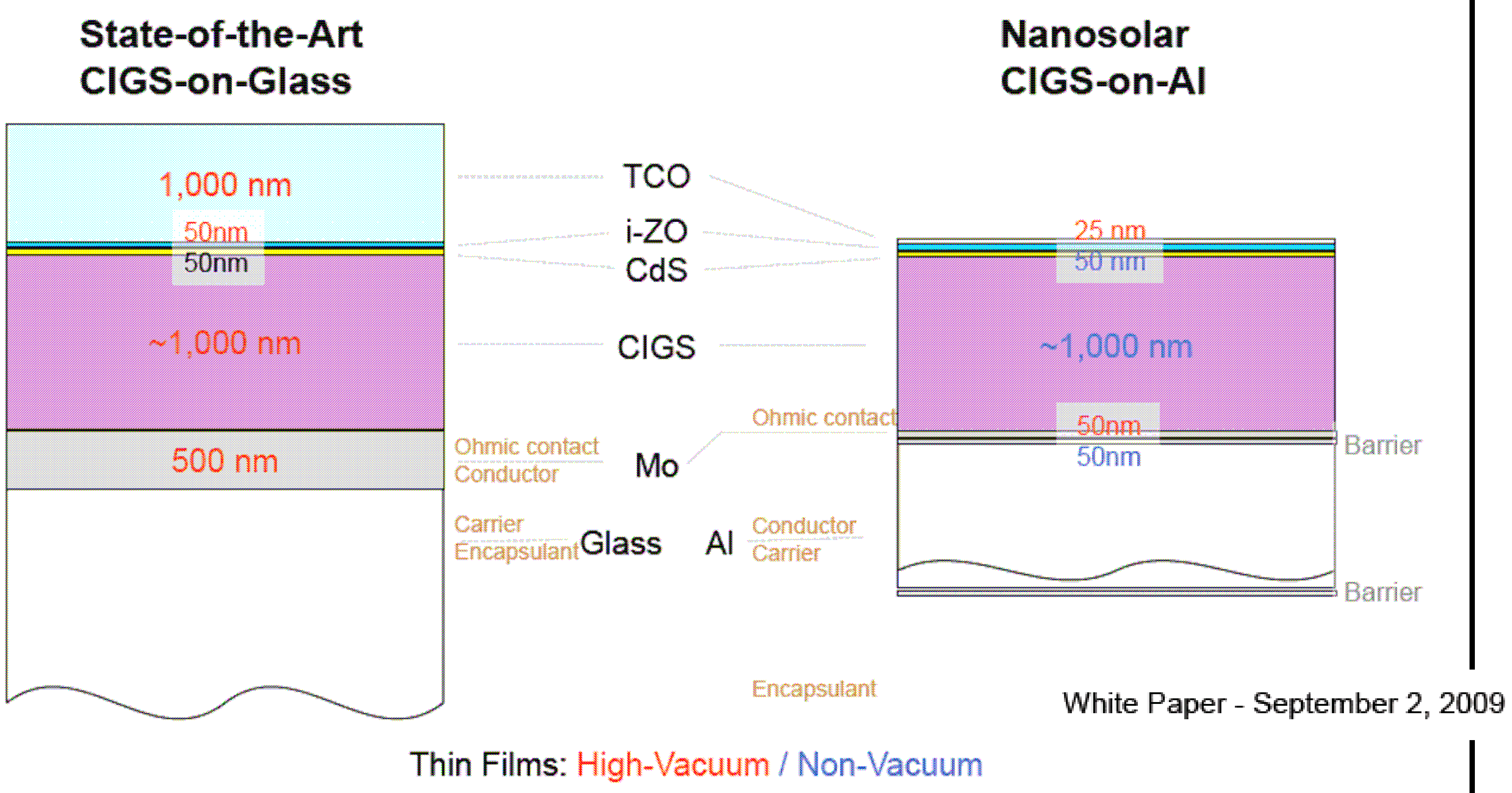

Figure 4: Comparison of State-of-the-Art CIGS versus Nanosolar's CIGS-on-Aluminum. Thickness numbers in red indicate depositions using a high-vacuum deposition technique. The state-of-the-art stack requires close to 3000nm of high-vacuum processing whereas Nanosolar's stack requires less than a tenth of that.

Souce: Nanosolar White Paper 2009

CIGS absorber layer from nanoparticle printing

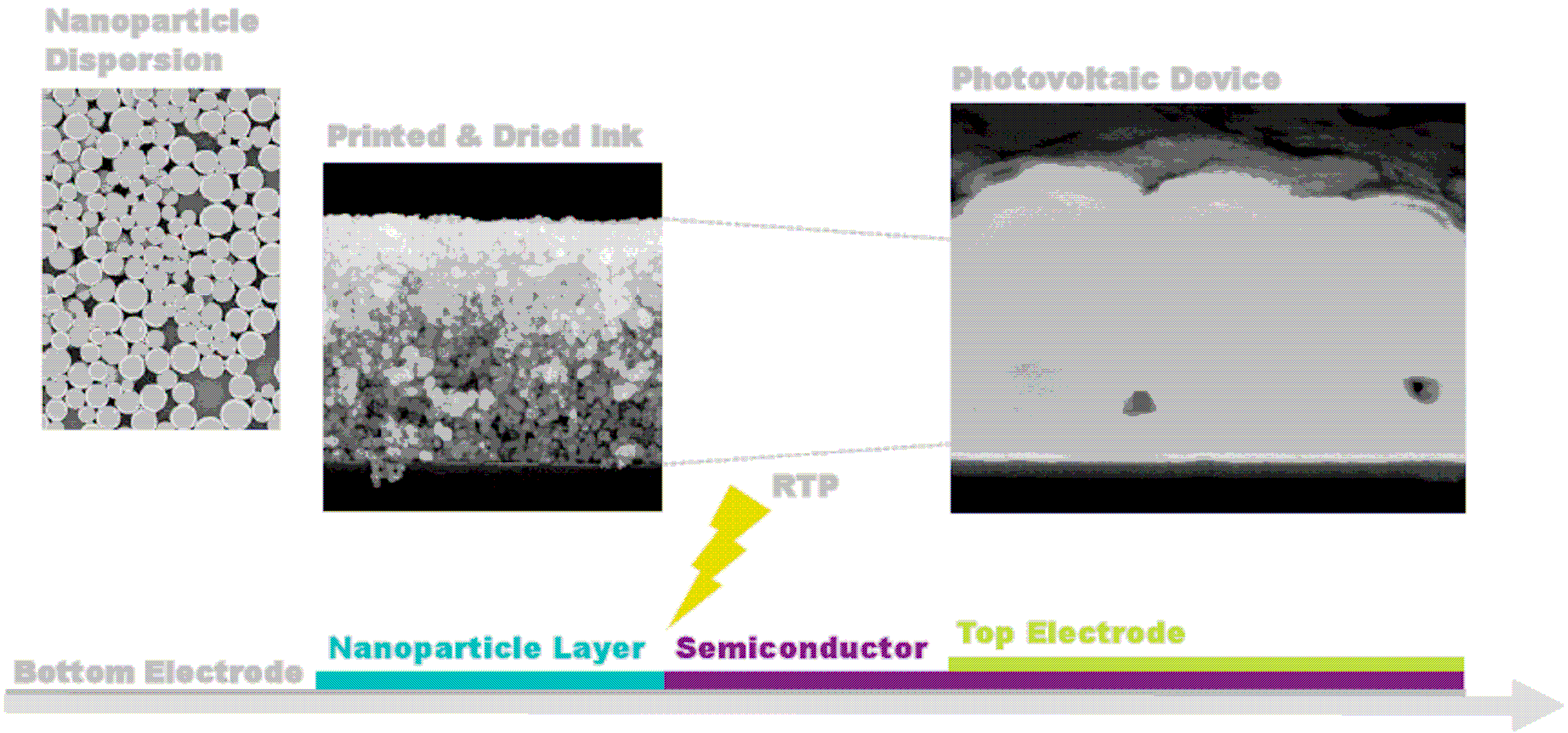

Figure 8: The basic process sequence consists of creating a high-quality dispersion of nanoparticles suitable for high-quality wet coating and converting the printed layer into a high-quality semiconductor using Rapid Thermal Processing (RTP). The art consists of doing so in a way that the resulting semiconductor is indistinguishable in electronic and crystalline quality from one deposited with far more expensive high-vacuum deposition techniques.

Souce: Nanosolar White Paper 2009

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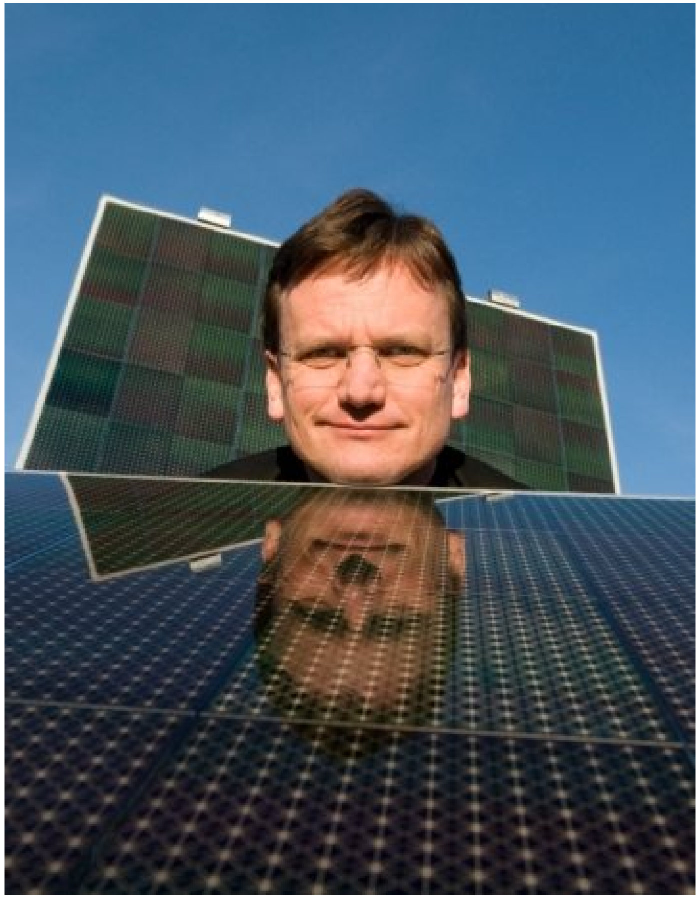
Nanosolar Ships First Panels - Dec. 18,2007



Martin Roscheisen, CEO

首批的三片量產太陽能板一片將掛在公司裡做「精神堡壘」，一片捐贈給聖荷西的科技博物館，一片拿到 eBay 上拍賣，起價 0.99 美元，3天後叫價到13,000美元。

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Ink Printing製備CIGS 吸收層

優點：

(1) **Cu、In、Ga、Se四成份控制較容易可直接做 pattern(模組)**

(2) 採用非真空製程以降低設備投資

(3) 提昇材料利用率 **>95% (Multi-source vacuum deposition只有 30%~60%)**

(4) **Throughput可達10-100X**

缺點：

(1) 奈米粒子製程複雜(需合成**nanoparticle**、加入**wetting agent**、**dispersion agent**分散於溶劑中，**printing**、烘乾去除溶劑、通H_2/N_2還原)

(2) 尚無供應廠商

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- *Dye Sensitized Solar Cell (DSSC)*
- *Organic PV (OPV)*

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The Cheapest Option

Efficiency: 0.3 %

We don't have the land and water to provide the world with energy this way.

Can we artificially improve the efficiency?

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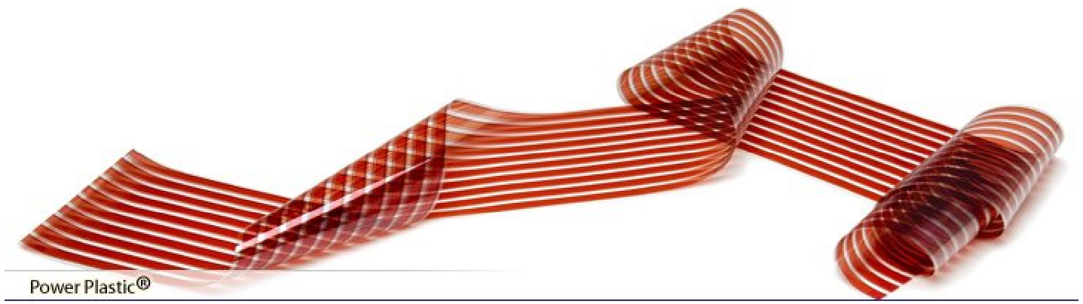
Konarka — Power Plastic



March 6, 2008

Konarka has developed its affordable Power Plastic film with several manufacturing techniques, from an early proprietary printing process (pictured above in image rotated for space) to a new breakthrough with inkjet printers that should dramatically reduce costs, with applications including sensors and RFID. (Photograph by David A. White/Konarka)

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➢*Organic PV (OPV)*

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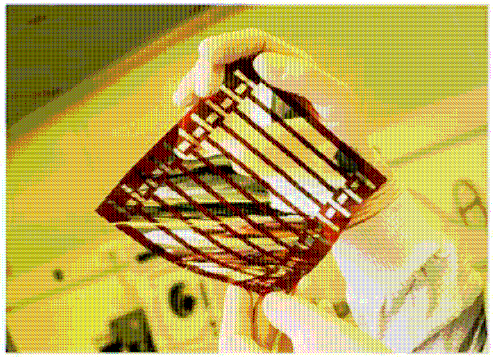
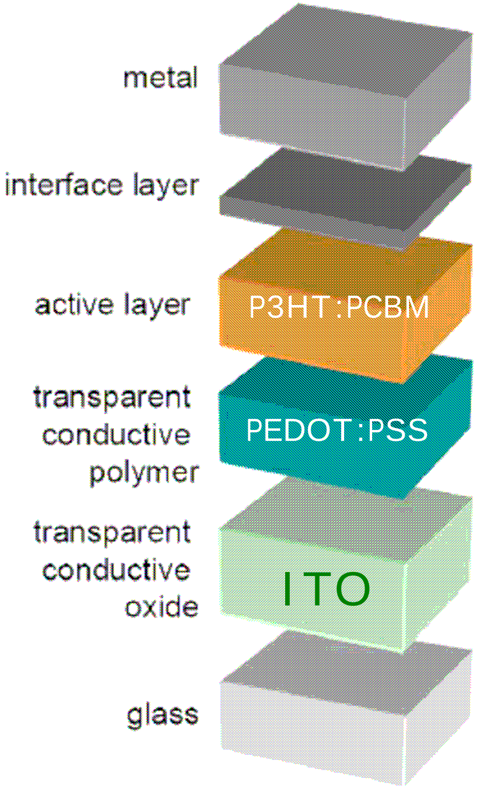
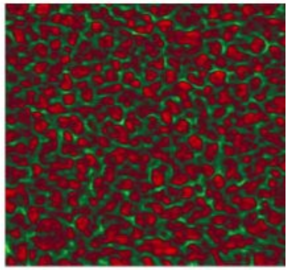
Polymer Solution Processed Solar Cells





Active layer

Polymer – fullerene

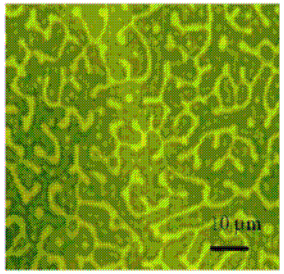


ITO/PEDOT:PSS/P3HT:PCBM/Al
η ~5% (Adv. Funct. Mater. 2005,15,1617)

ITO/PEDOT:PSS/P3HT:PCBM/TiO_2/Al
η ~5.8% (MRS 2006)

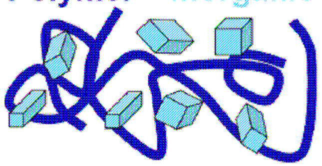
ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al:
η ~6.1% (APL 2007,90,163511)

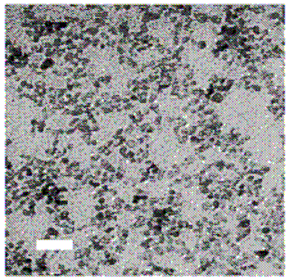
Polymer – polymer



P3HT:F8TBT: η ~1.8%
(Appl. Phys. Lett. 2007,90,193506.)

Polymer – inorganic





P3HT:CdSe nanorod: η ~1.7%
(Phys. Chem. Chem. Phys. 2006,8,3557.)

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Donor and Acceptor

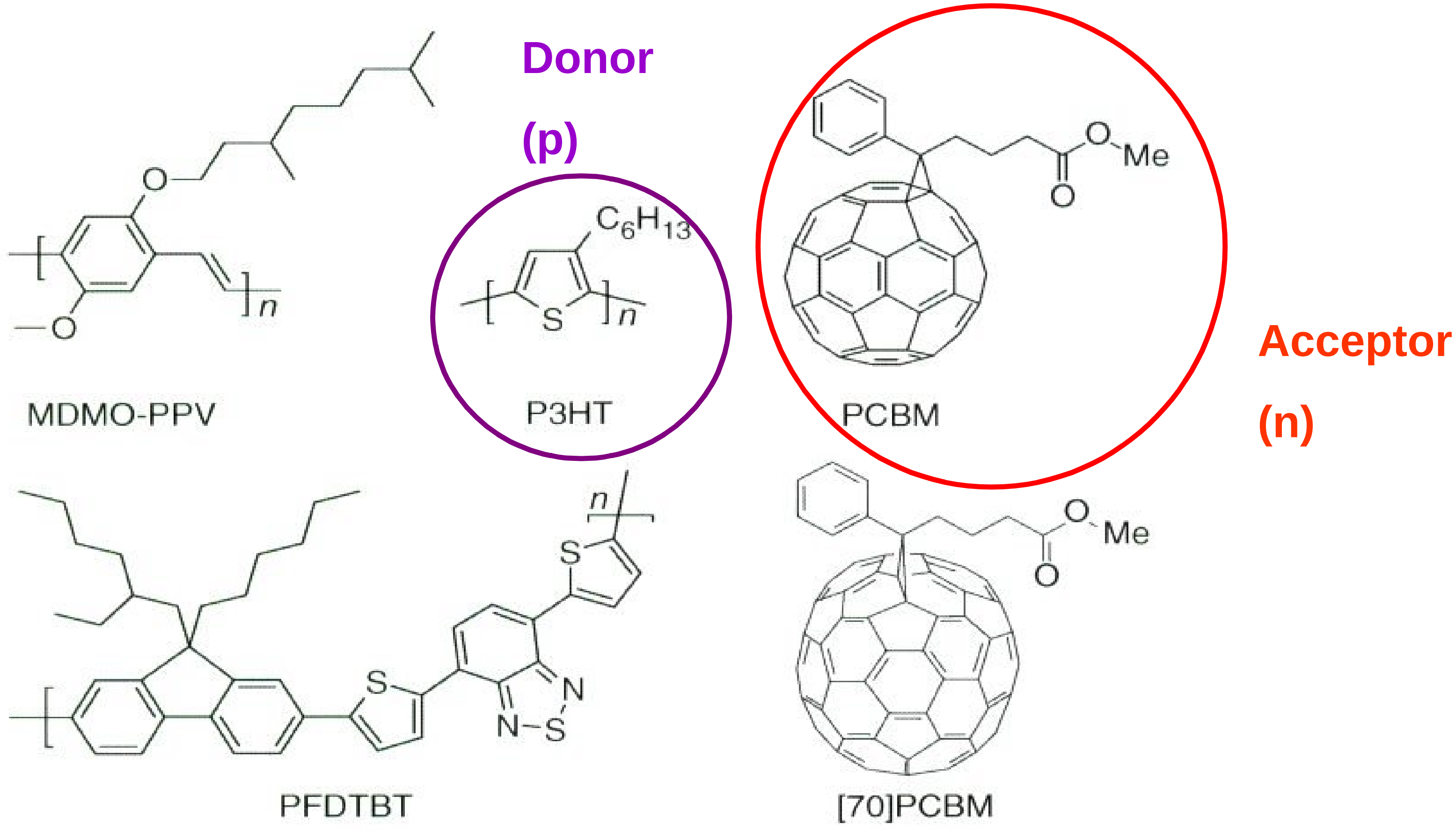

Chart 1. Donor and acceptor materials used in polymer–fullerene bulk heterojunction solar cells. Donors: MDMO-PPV = poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-p-phenylene vinylene]; P3HT = poly(3-hexylthiophene); PFDTBT = poly[2,7-[9-(2′-ethylhexyl)-9-hexylfluorene]-alt-5,5-(4′,7′-di-2-thienyl-2′,11′,3′-benzothiadiazole)]. Acceptors: PCBM = 3′-phenyl-3′H-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3′-butanoic acid methyl ester; [70]PCBM: 3′-phenyl-3′H-cyclopropa[8,25][5,6]fullerene-C_{70}-D_{5h}(6)-3′-butanoic acid methyl ester.

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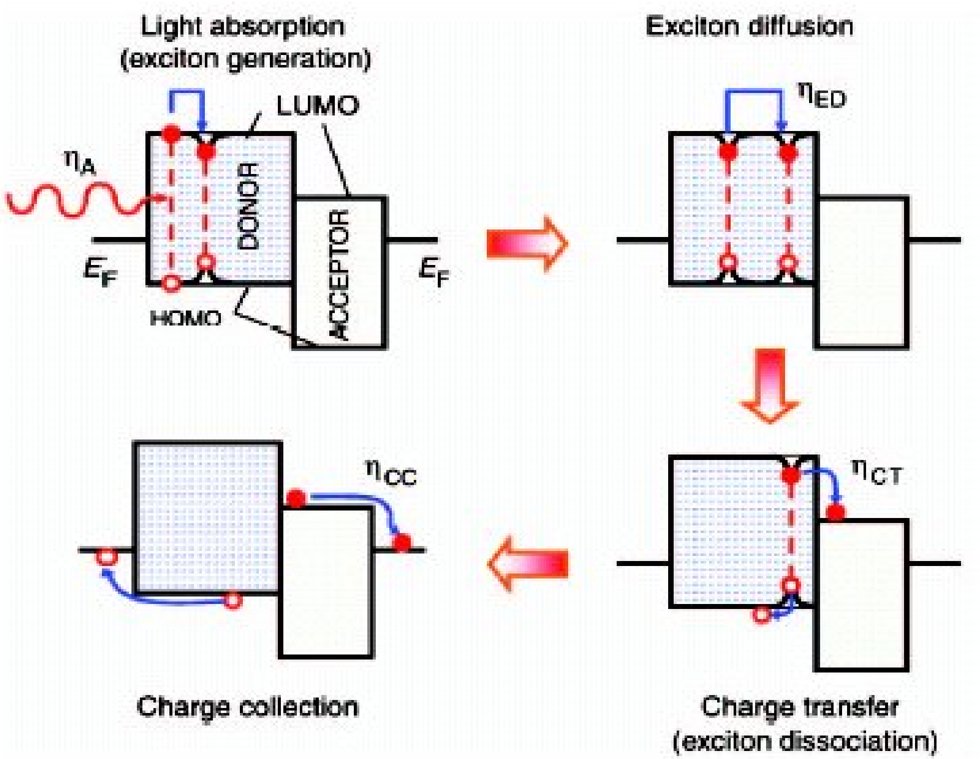
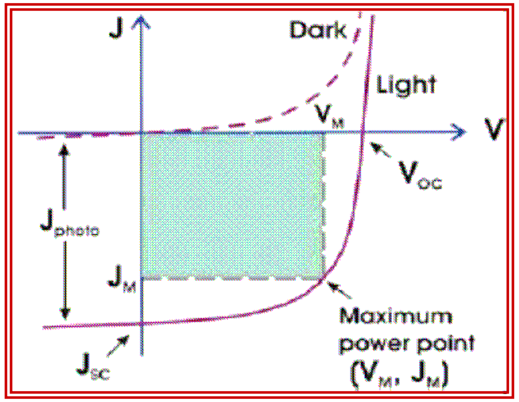
Requirements for High Efficiency

1. **Efficient light harvesting**
2. **Ultrafast photoinduced charge separation**
3. **Suppression of the back-charge-transfer so as to allow sufficient time to collect the separated charges at electrodes prior to recombination**
4. **Efficient collection of the separated charges at the electrodes**





$$\eta_j = \eta_{abs} \times \eta_{diss} \times \eta_{out}$$

$$= JmVm/Psun$$

$$= 100 * Jsc * Voc * FF/Psun$$

$$FF = JmVm/JscVoc$$

Psun = A x (W/m²)

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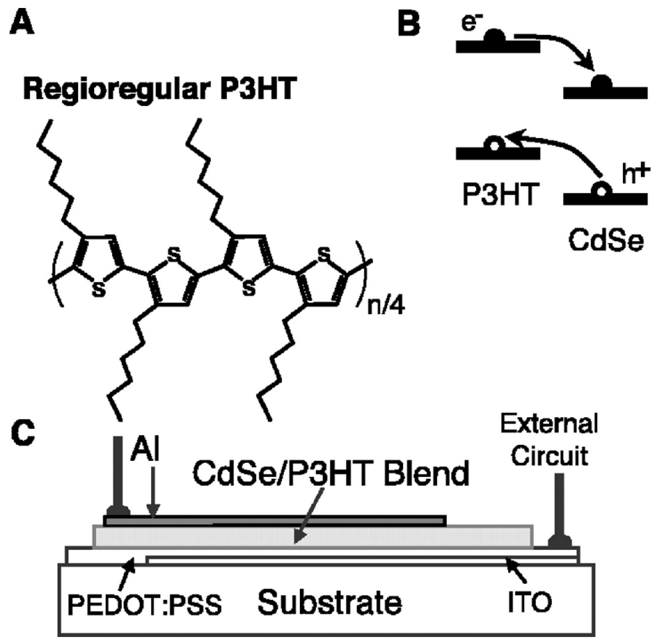
Polythiophene/CdSe Nanorod



A. poly (3-hexylthiophene)高分子(P3HT)結構 (Donor層材料)
B. CdSe Nanorod與P3HT能階圖顯示：
電子在CdSe層傳輸；電洞在P3HT層傳輸。
C. CdSe Nanorod Solar Cell元件結構圖：CdSe/P3HT混合層厚度約200 nm (90wt%的CdSe Nanorod與P3HT混合，再以三氯甲烷加熱溶解成溶液狀、Spin Coating成膜)，夾於鋁電極與透明導電電極(PEDOT:PSS)間。

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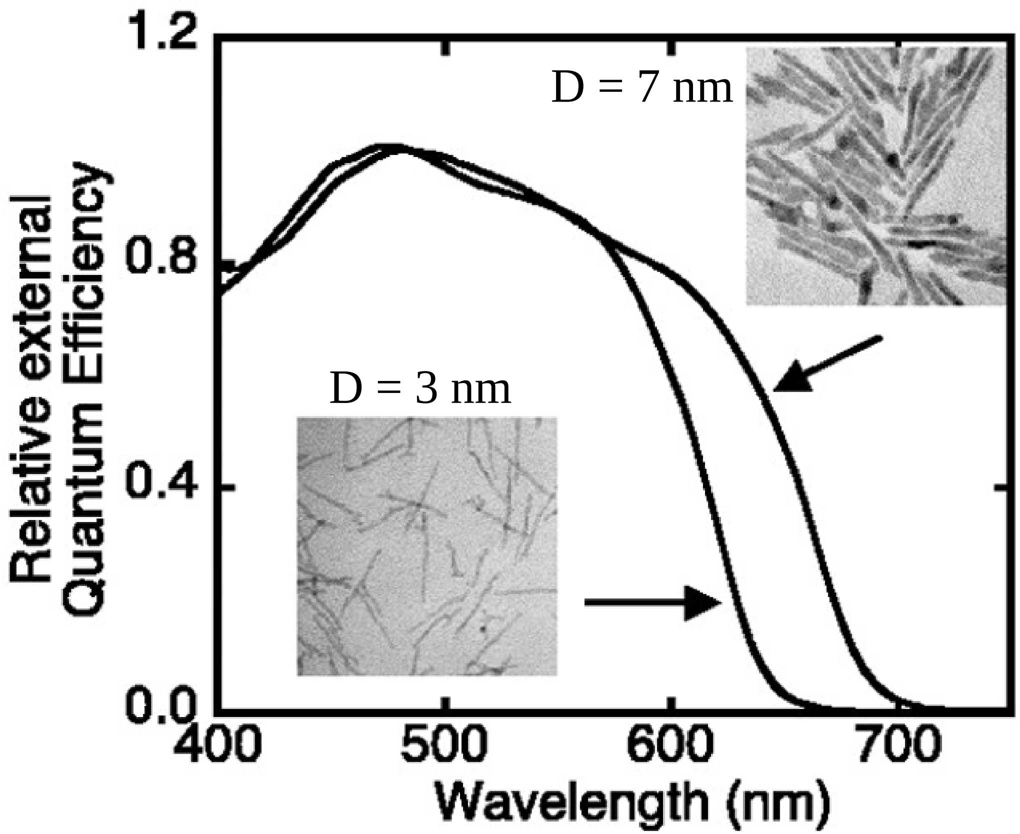
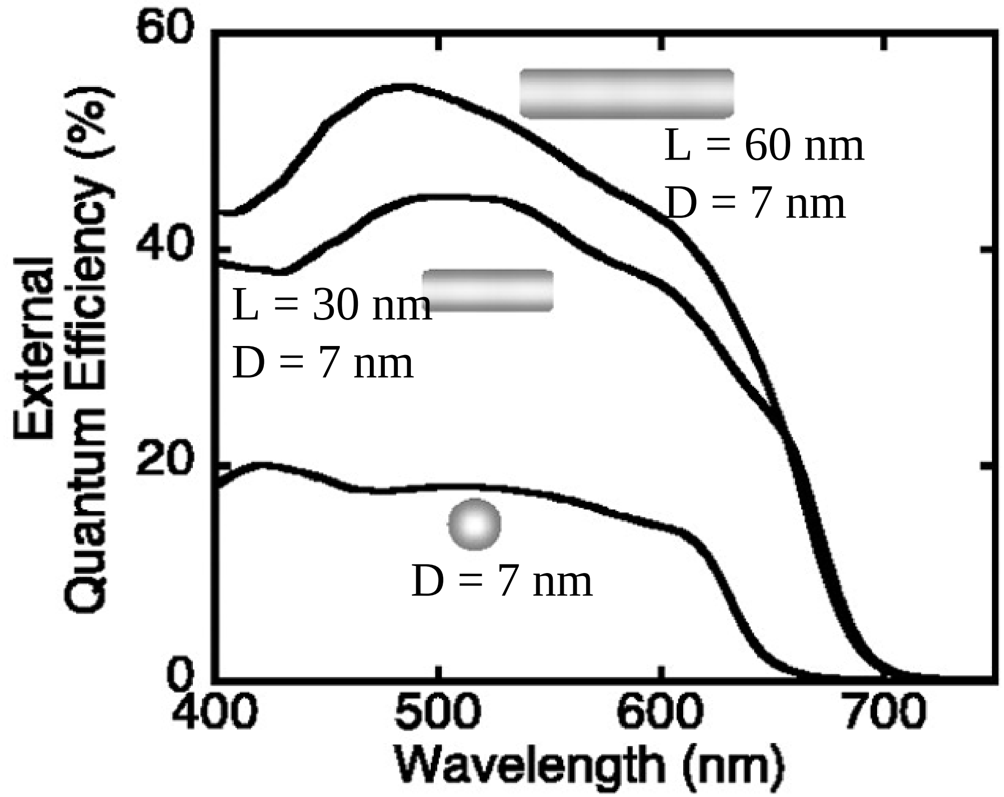
CdSe Nanorod直徑對吸收光譜之效應



改變Nanorod的直徑，使Band Gap改變至與太陽光譜重疊，可增加發電效率。

Photocurrent spectra。固定Nanorod的長度為60 nm時，不同直徑會有不同的光電子光譜。

CdSe Nanorod長度對吸收光譜之效應



控制Nanorod的長度，可改變電子於薄膜元件中的遷移距離、增加電子遷移速率而增加發電效率。

當Nanorod直徑為7 nm時，CdSe Nanorod / P3HT混合層可吸收300～720 nm的光。於此結構之元件中，不同長度的Nanorod有不同的External Quantum Efficiency。

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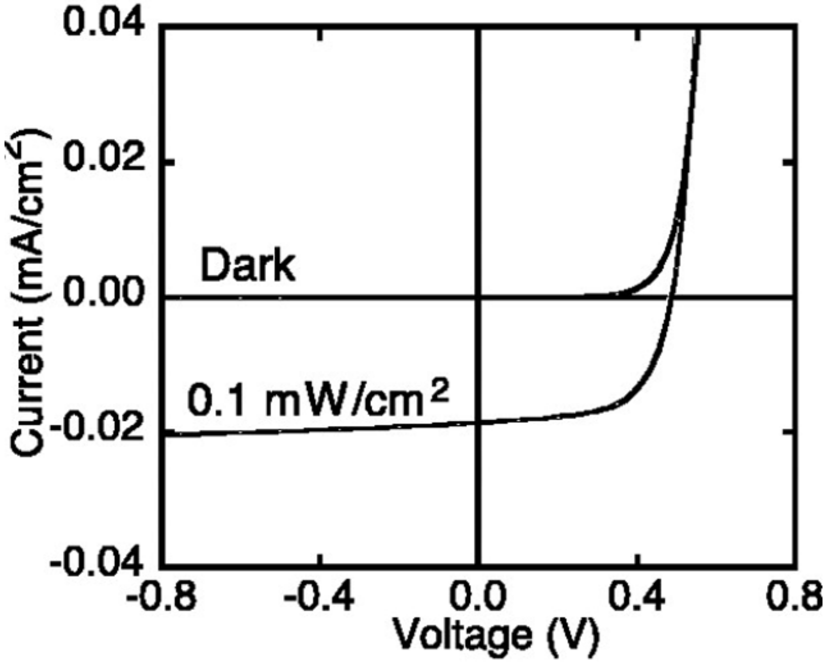
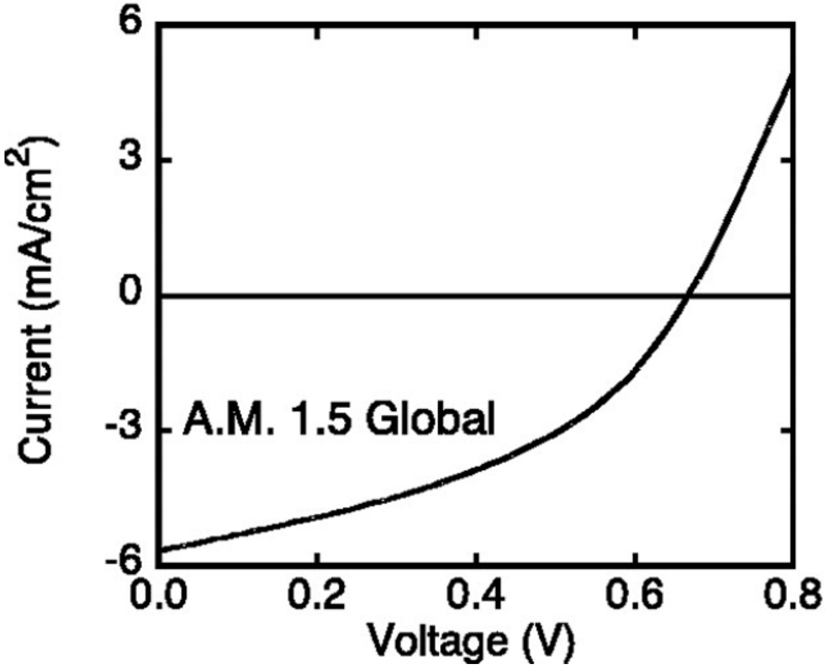
CdSe/P3HT太陽電池之效率





Nanorod直徑7 nm，長60 nm的元件，以波長515 nm、功率0.083 mW/cm^{2}的光源照射所得之I-V curve。所測得之I_{sc} = 0.019 mA/cm^2、Power Conversion Efficiency為6.9 %。

Nanorod直徑7 nm，長60 nm的元件，以AM 1.5 Global光源照射所得之I-V curve。所測得之v_{oc} = 0.7 V、Power Conversion Efficiency為**1.7 %**。

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➢ *Dye Sensitized Solar Cell (DSSC)*

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Prof. Michael Grätzel

瑞士洛桑聯邦理工學院(EPFL, Switzerland) Grätzel教授仿效大自然中植物體能夠藉由綠葉中的葉綠素，在吸收太陽光的情況下，將光能轉變成化學能的特性，於1991年發表染料敏化太陽能電池 (Dye Sensitized Solar Cell, DSSC) 的原型

Ref. : Grätzel, M. et al., *Nature*, 335, p.737, 1991
Patent: US Patent 4,927,721, May 1990
US Patent 5,084,365, Jan 1992

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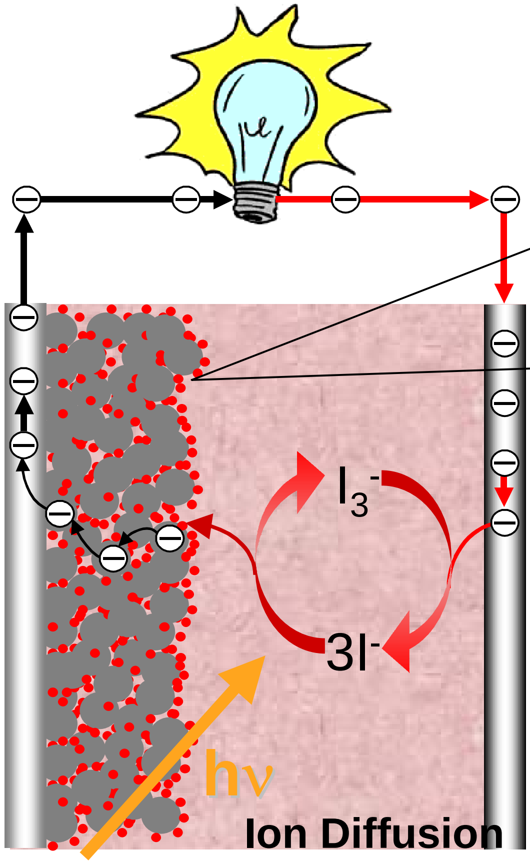
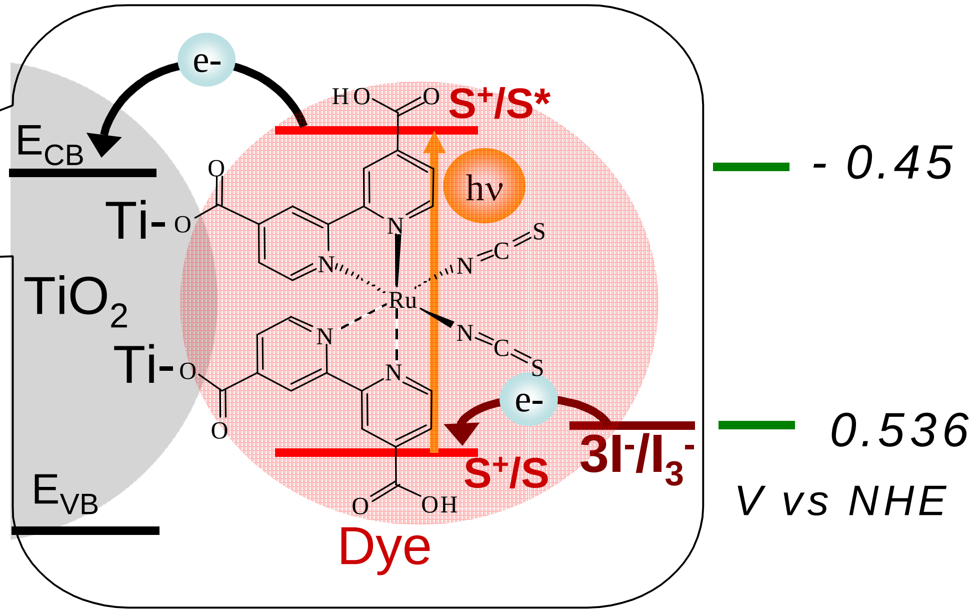
染料太陽電池原理與關鍵技術

染料太陽電池工作原理





$$
\begin{array}{lll}
\textit{Anode}: & S + h\nu \rightarrow S^* & \text{Absorption} \\
 & S^* \rightarrow S^+ + e^-(TiO_2) & \text{Electron injection} \\
 & 2S^+ + 3I^- \rightarrow 2S + I_3^- & \text{Regeneration} \\
\textit{Cathode}: & I_3^- + 2e^-(Pt) \rightarrow 3I^- & \\
\textit{Cell}: & e^-(Pt) + h\nu \rightarrow e^-(TiO_2) &
\end{array}
$$

M. Grätzel, Nature 2001, 414, 338–344.
B. O'Regan, M. Grätzel, Nature 1991, 353, 737–740

高效率的染料敏化太陽電池需求

1. 高比表面積TiO_2電極
2. 具適當HOMO-LUMO電位、低bandgap的染料
3. 高催化能力的陰極電極
4. 快速氧化還原能力電解質
5. 寬工作電壓的溶劑

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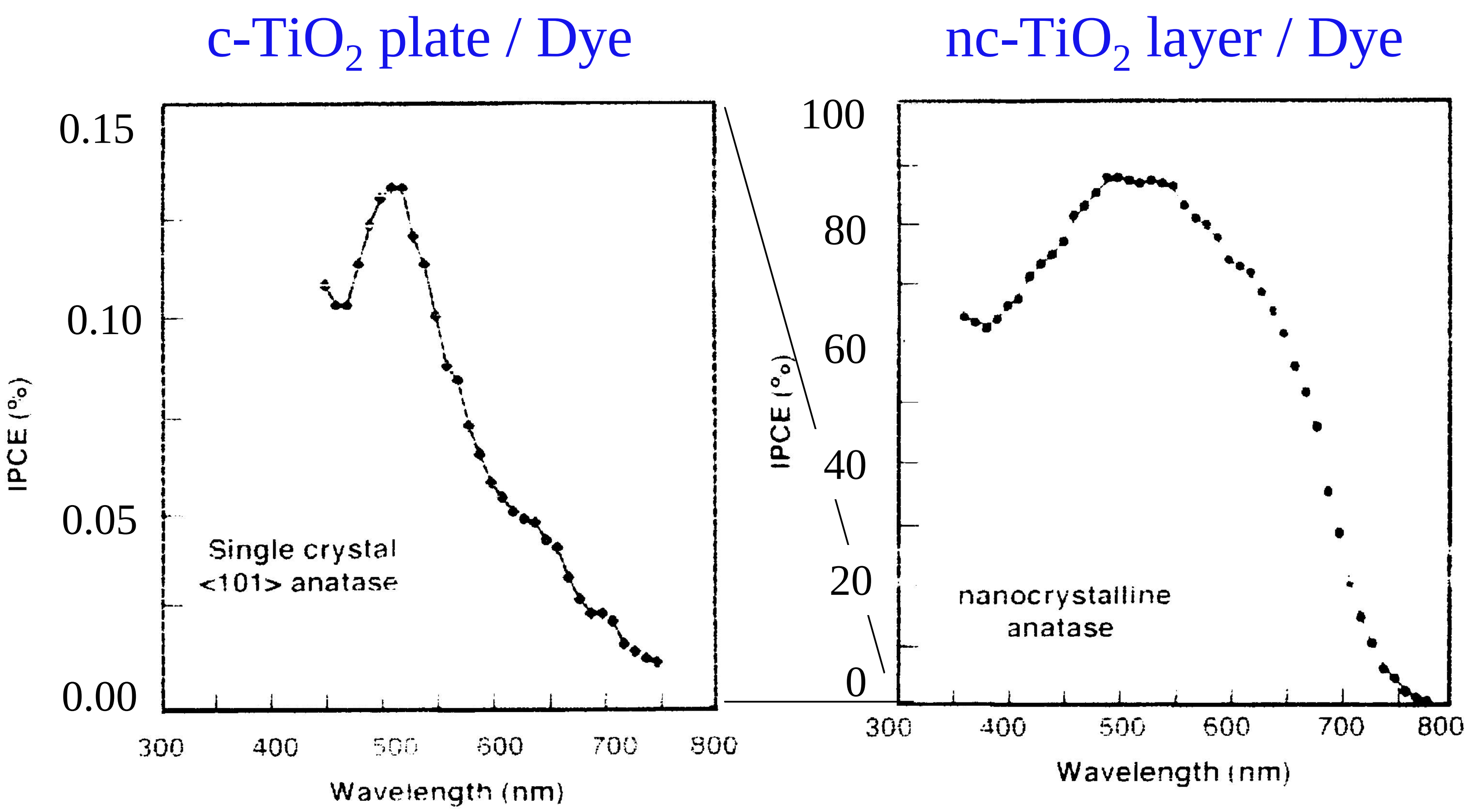
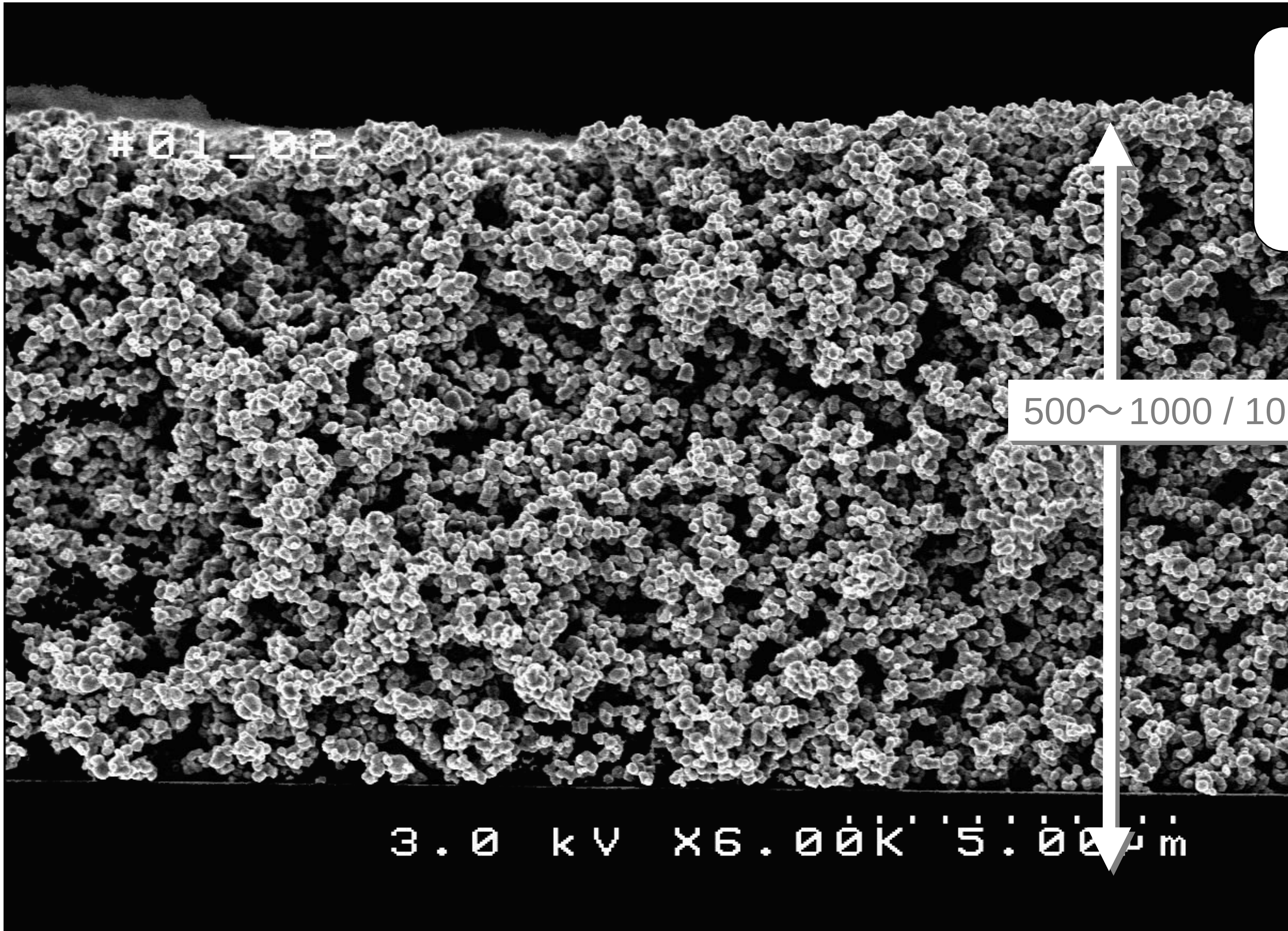
Surface enhancement by nc-TiO_2

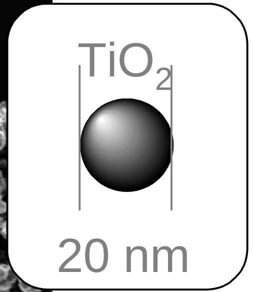
Photocurrent ×1000!



Source: *Prof. Uchida's lecture*

TiO_2 nano crystalline film





Source: *Prof. Uchida's lecture*

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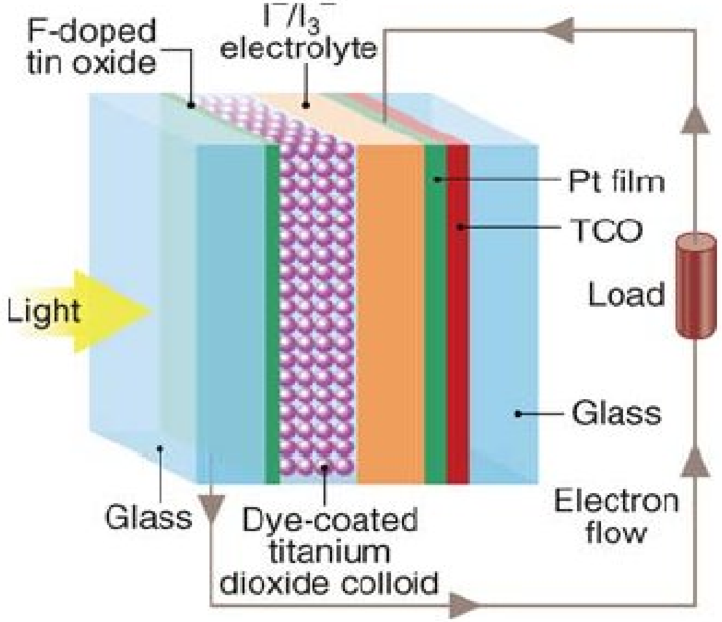
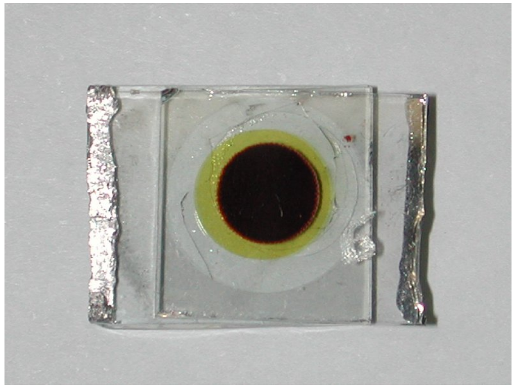
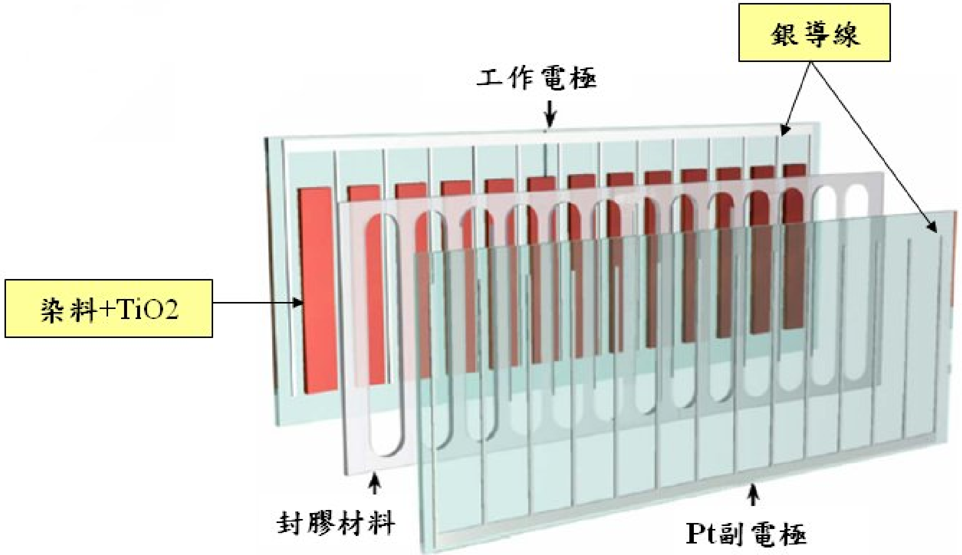
Cell structure of DSSC

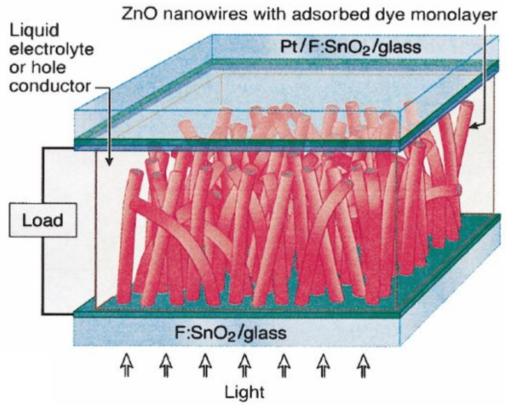


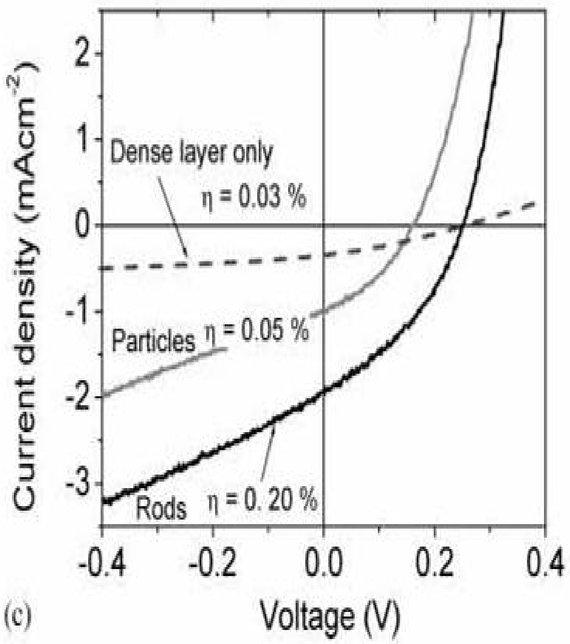


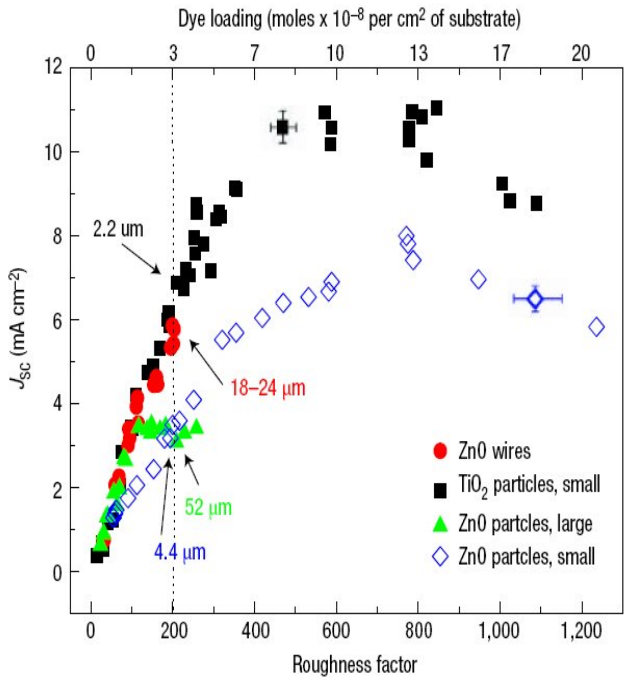


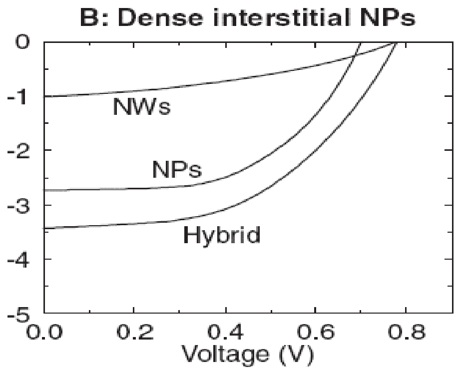
Nanowire Dye-sensitized Solar Cell

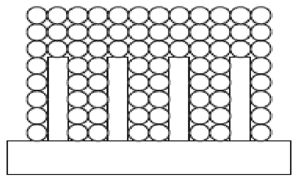
- UC Berkeley/LBNL, UC Santa Barbara/U. Minnesota, EPFL/Imperial College (2005,2006).
- Nanowires provide better connectivity for electrons transport, results in slower recombination.
- Nanowire can't provide large enough surface area for more photoexcited electrons, results in small fill factor and so small efficiency.









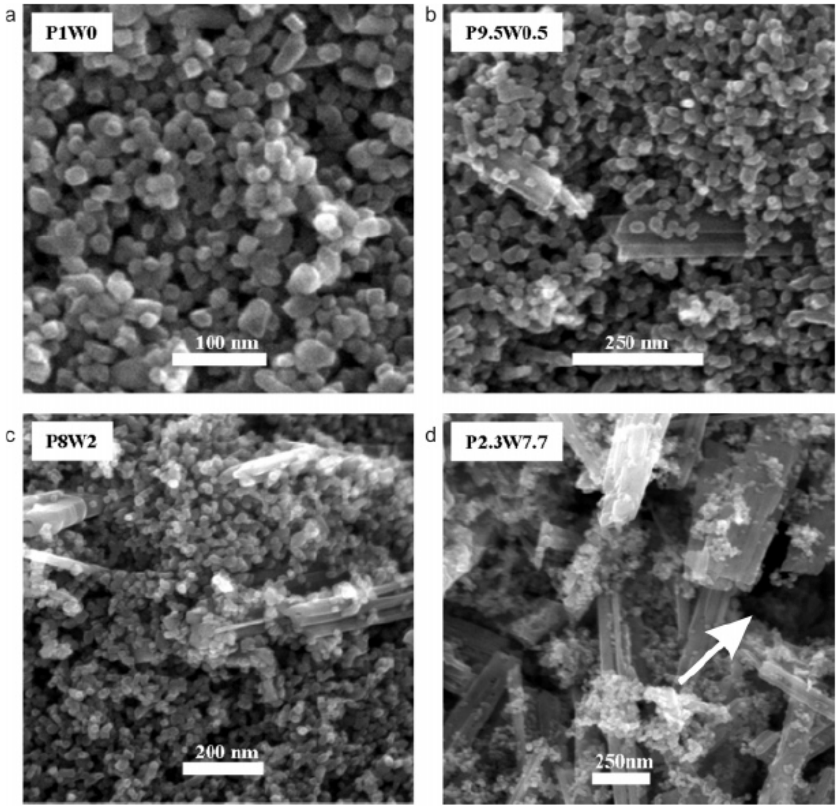


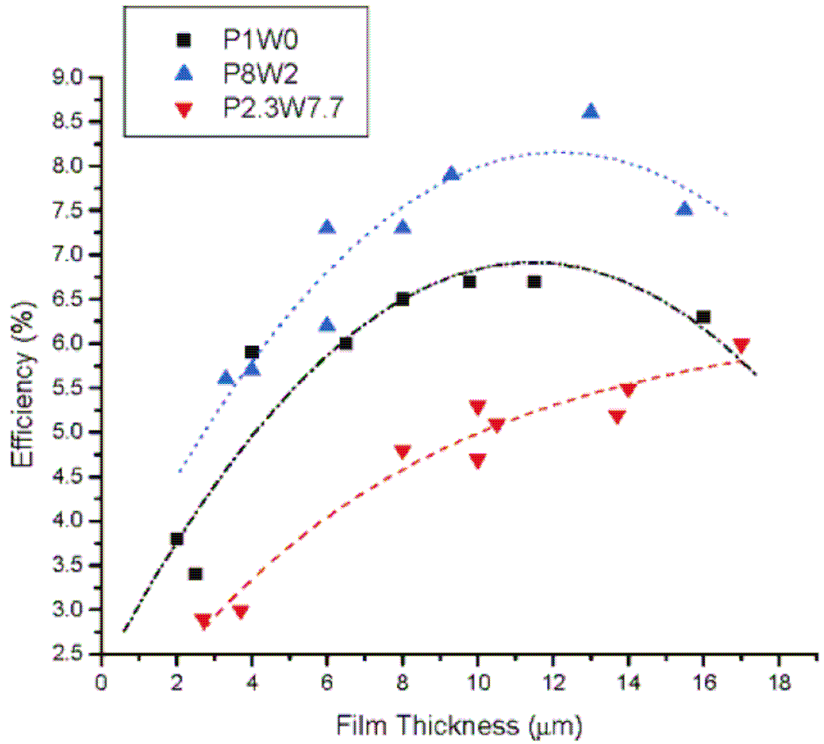
Nanorod on polymer DSC
J. Phys. Chem. (2006),EPFL/Imperial

Comparison of nanowire and nanoporticle
Nature Materials(2005),UCB

Hybrid nanowire/nanoparticle DSC
Solar Energy Materials & Solar Cells (2006),UCSB/UM

DSSC with NPs & NWs composites





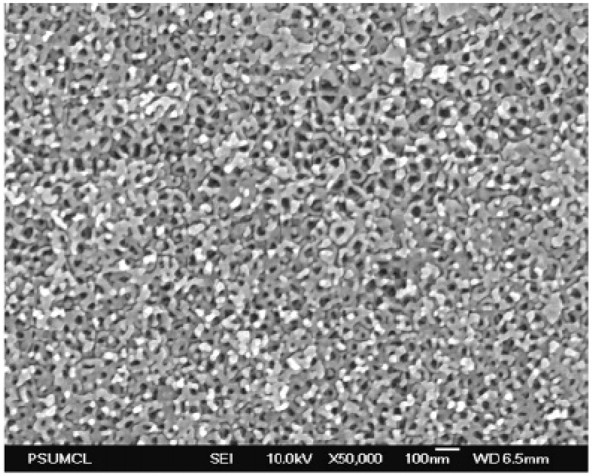
P1W0：100% NPs

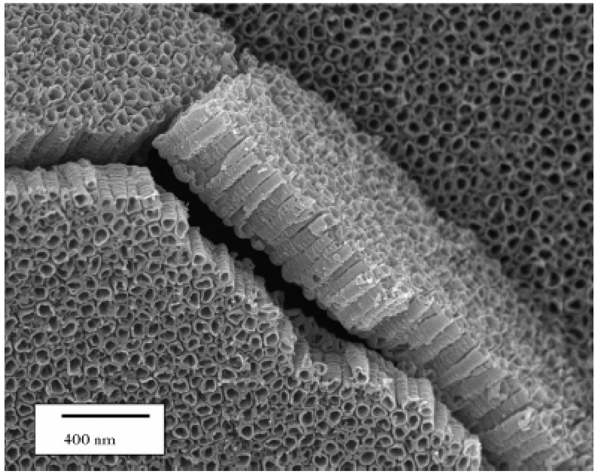
P8W2：80%NPs, 20%NWs

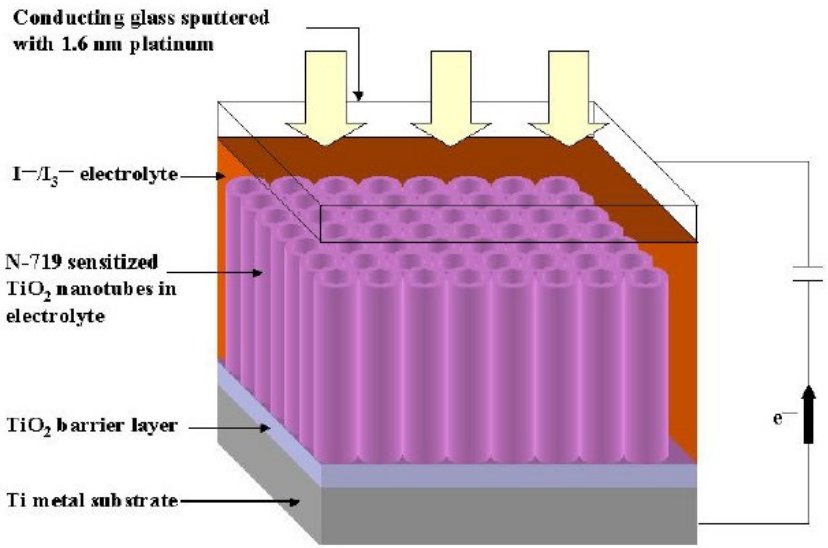
P2.3W7.7：23%NPs,77%NWs

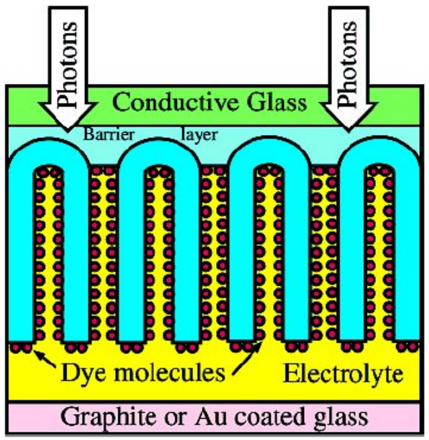
J. Phys. Chem. B, 110(2006) 15932

Titanium nanotubes





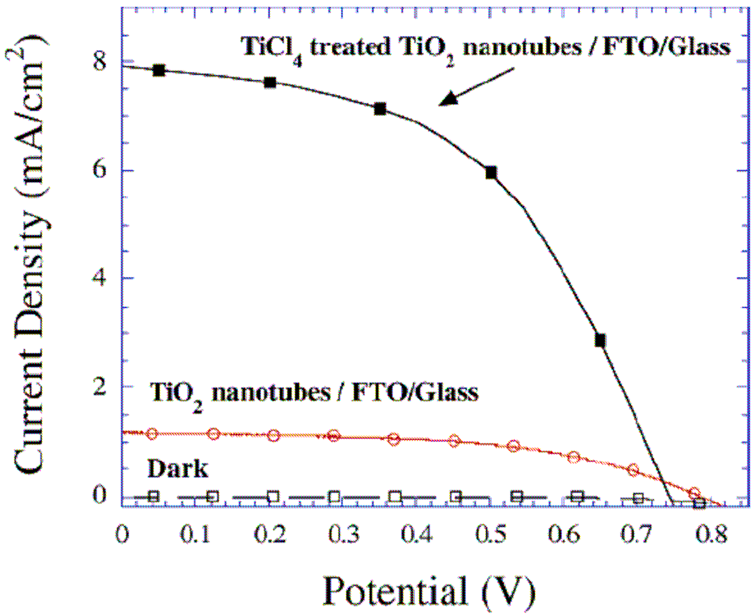




Nano. Lett., 6 (2) (2006) 215-218.

a 500-nm-thick Ti thin film (sputtered onto SnO_2:F coated glass at 500 °C) anodized using a 0.5% HF electrolyte concentration at a potential of 12 V.

Titanium nanotubes DSSC



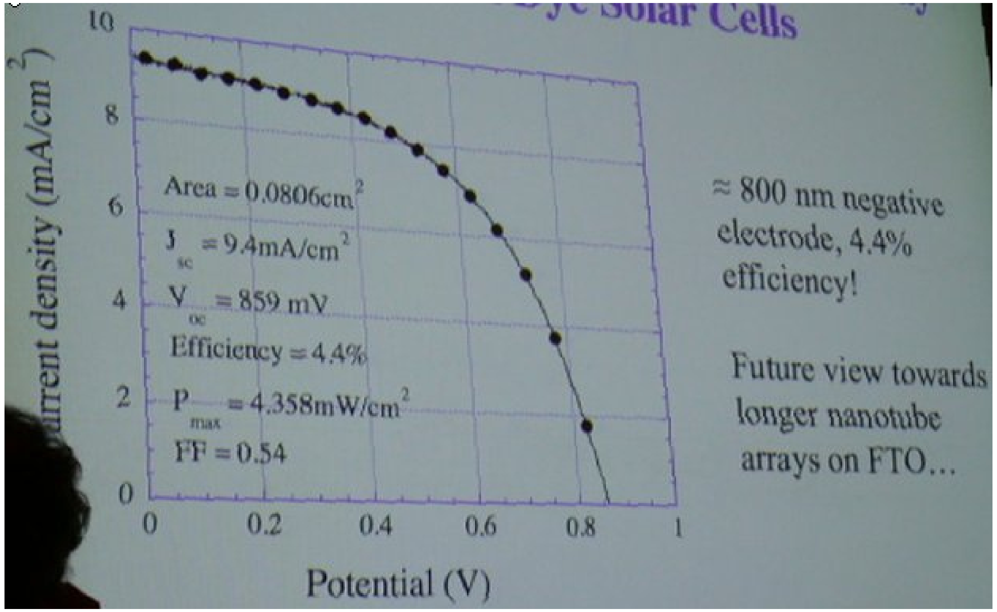
360nm negative electrode

Jsc = 7.87mA/cm^2

Voc=0.75V

Efficiency=2.9%

FF=0.49



1. *Nano. Lett.*, 6 (2) (2006) 215-218.
2. 2006 *MRS spring meeting*.

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Dye-sensitized ZnO & TiO_2 solar cell

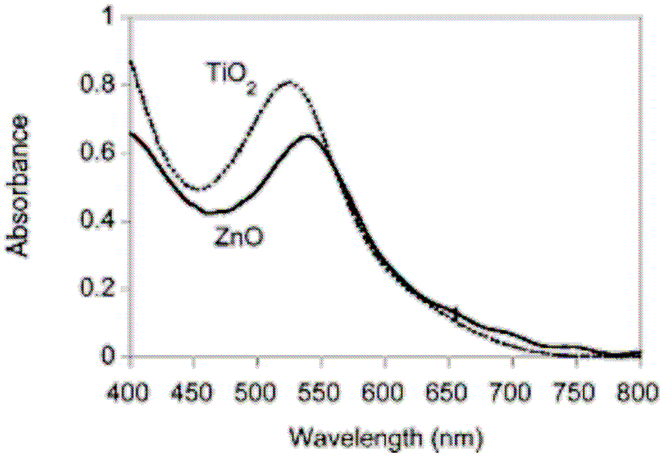
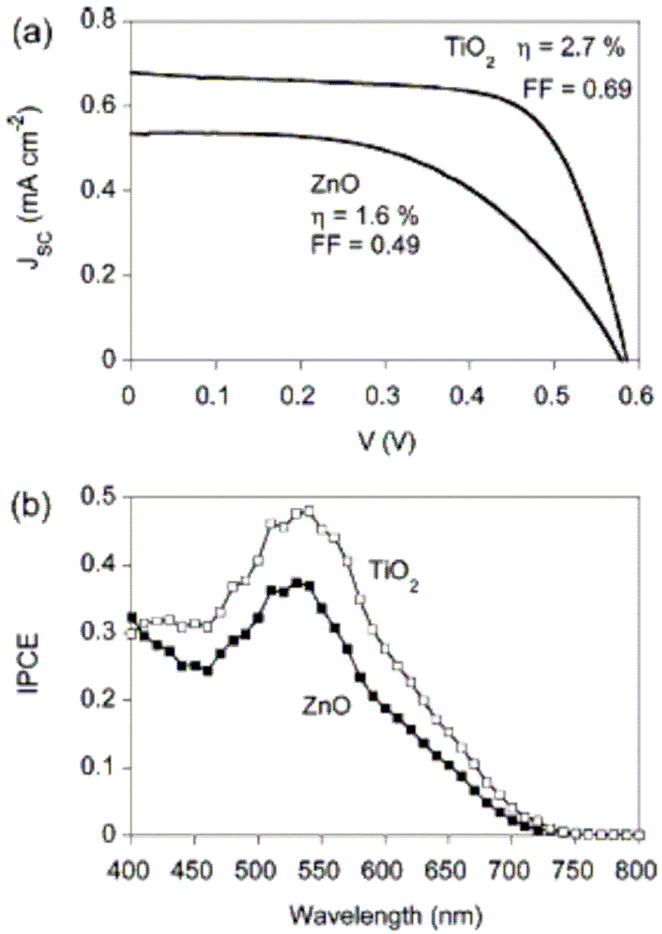


Figure 3. Absorption spectra of N719 dye adsorbed on ZnO and TiO_2 films (thickness 4 μm). The spectra are corrected for ZnO, TiO_2, and substrate absorption.

Zn^{+2}/dye complex formation



J. Phys. Chem. C, 111 (2007) 1035

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ZnO "Popcorn Ball" DSSC

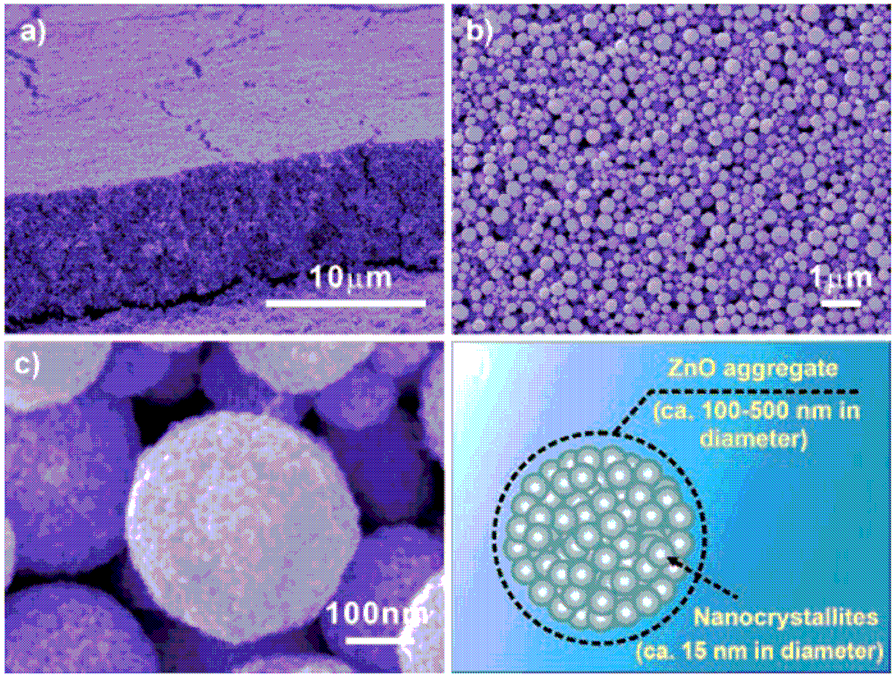
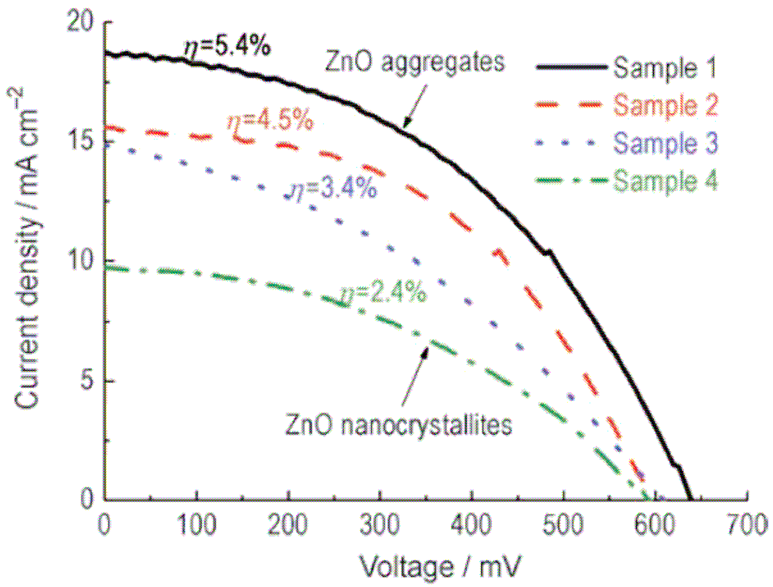


Figure 1. Morphology and structure of the ZnO aggregate film. a) SEM image of the cross section of the ZnO aggregate film. b) SEM image of the top view of the ZnO film consisting of polydisperse aggregates. c) A magnified SEM image of an individual ZnO aggregate. d) A schematic diagram that illustrates the microstructure of aggregated ZnO comprising closely packed nanocrystallites.



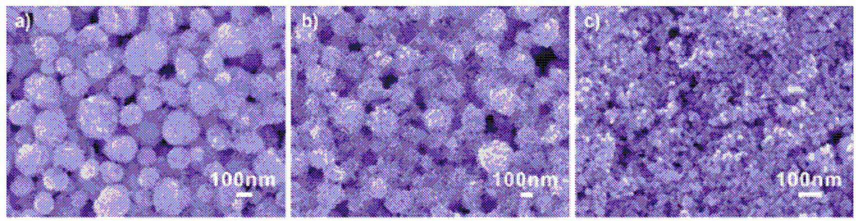


Figure 2. SEM images showing the morphology evolution of ZnO films synthesized at different temperatures: a) 170°C (sample 2), b) 180°C (sample 3), and c) 190°C (sample 4).

Angew. Chem. Int. Ed., 47 (2008)

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Gifu University

PLASTIC SOLAR CELLS EMPLOYING ELECTRODEPOSITED ZNO AND ORGANIC PHOTOSENSITIZER DYES

Tsukasa Yoshida[1], Masaki Matsui[1], Kazumasa Funabiki[1], Hidetoshi Miura[2] and Yoshiya Fujishita[3]
[1] Center of Innovative Photovoltaic Systems (CIPS), Gifu University, Japan, [2] Chemicrea Inc., Japan, [3] Sekisui Jushi Corp., Japan

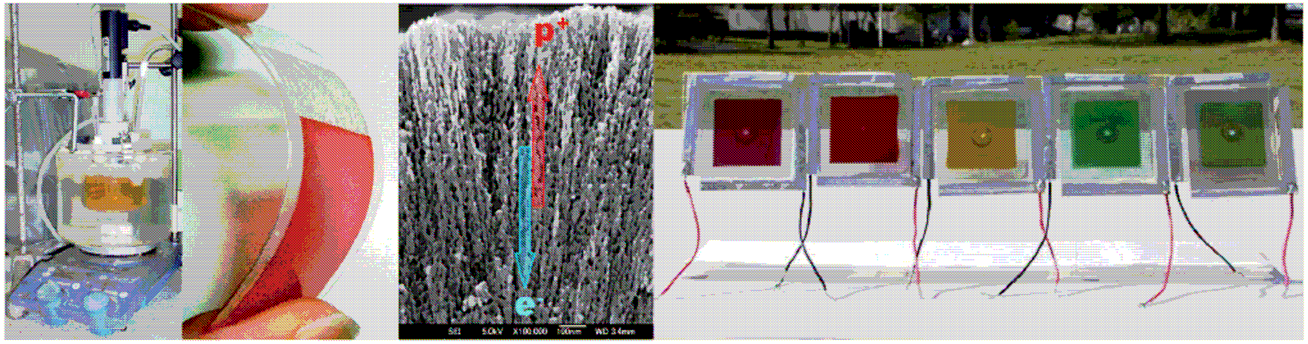

Fig. 1 Electrodeposition bath employing RDE, ZnO/eosinY hybrid thin film electrodeposited on ITO coated PET film, nanowire porous structure of electrodeposited ZnO thin film (cross section SEM) and colorful plastic solar cells (from left to right).

η =5.6% for small cell

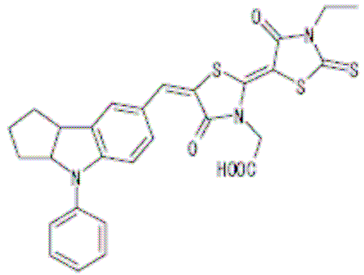

Fig. 2 The structure of new DN-7 dye.

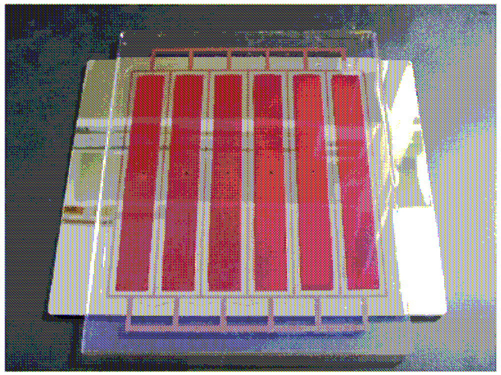

Fig. 3 Full plastic submodule (10 cm × 10 cm) with promising 3.2% conversion efficiency (active area) employing electrodeposited ZnO and organic photosensitizer dye.

Technical Digest of the International PVSEC-17, Fukuoka, Japan, 2007

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Industrialization & Applications

工業技術研究院
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CIGS Potential Application

Solar Farms	*Low Cost*
BIPV	*Art & Reliability*
Rooftop	*High efficiency*
Portable or Customer Design	*Flexible*

CIGS Meets all application

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染料敏化太陽電池的應用

汽車天窗

Aisin精機的大面積模板與
「Toyota 夢的住宅PAPI」

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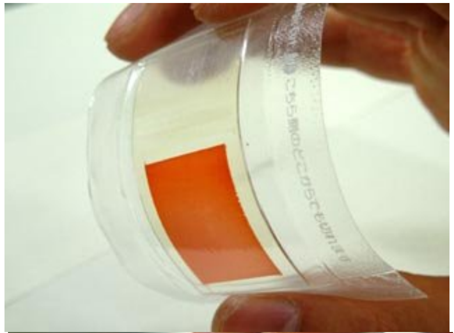
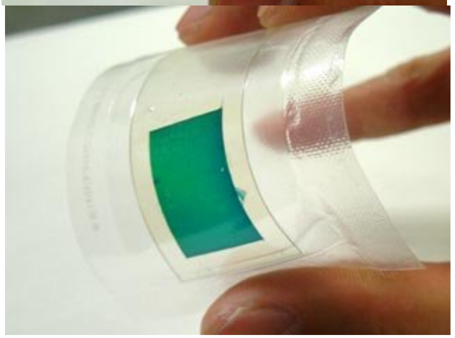
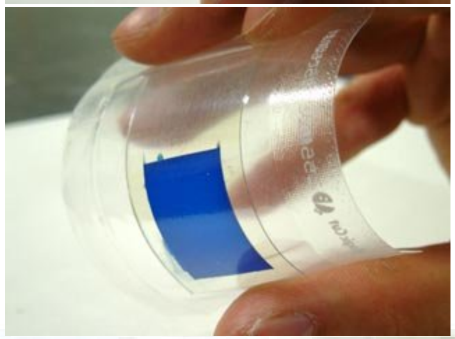
Features of DSSC







RAINBOW CELL

手機充電器

G24 Innovations, UK

Graetzel-type
"Roll to Roll" process
Plastic Modules

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CEATEC JAPAN – TDK

2008.10

TDK展出柔性色素增感型太陽能電池，在ZnO類電池中轉換效率最高。

Source: Nikkei Business Publications

Sony-Lanterns Using DSSC-Eco-Products 2008

Demonstration of a fan powered by the solar panel

Source: M. Kawai, Nikkei Microdevices, Dec. 12, 2008

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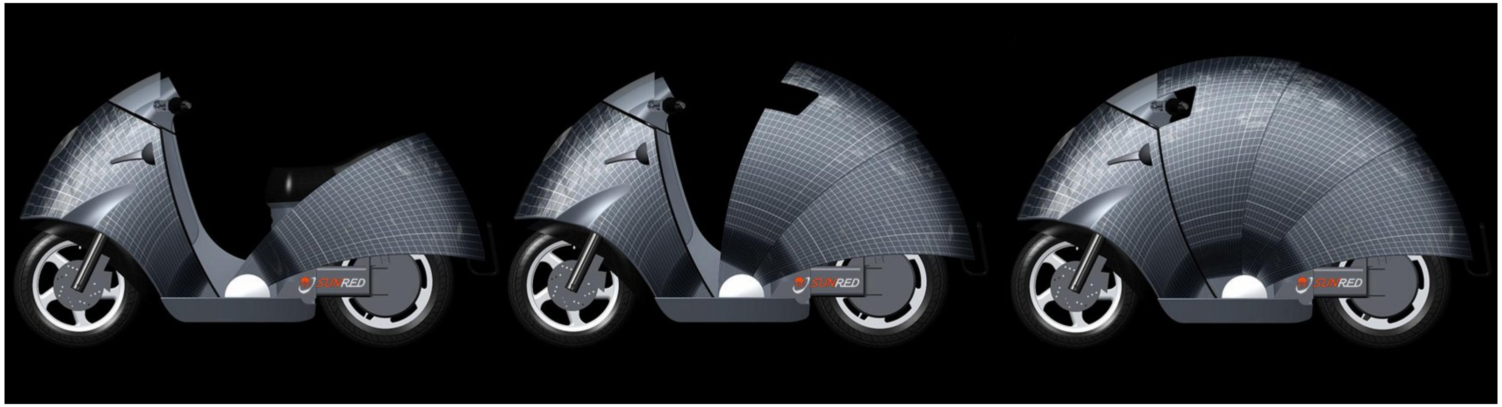
Moto Solar Urbana太陽能機車



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Thank You
for
Your Attention