



# **Solar Cells**

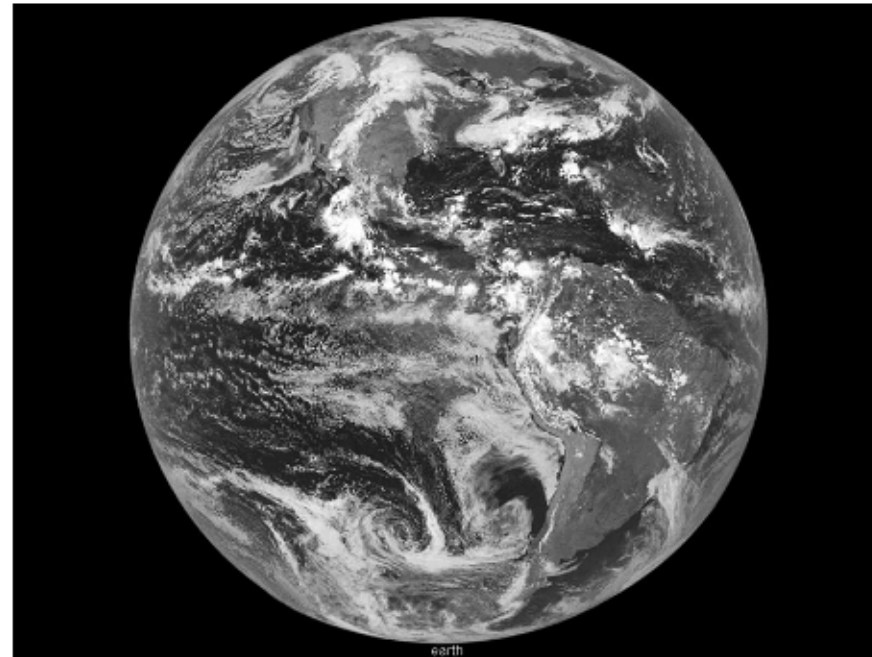
**Jong Hak Kim  
Chemical Engineering  
Yonsei University**

# Energy Problem

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## Humanity's 10 Problem for next 50 years

1. Energy
2. Water
3. Food
4. Environment
5. Poverty
6. Terrorism & War
7. Disease
8. Education
9. Democracy
10. Population



2003 6.3 Billion People  
2050 9-10 Billion People

**Nobel laureate Richard Smalley  
Houston in 2003**

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# Why Solar Cells ?

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If installed 5kWp solar array for a typical home, over a single year, it would prevent:

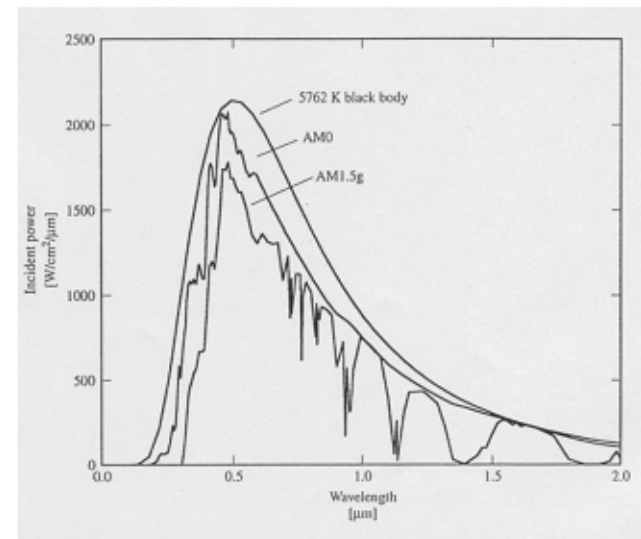
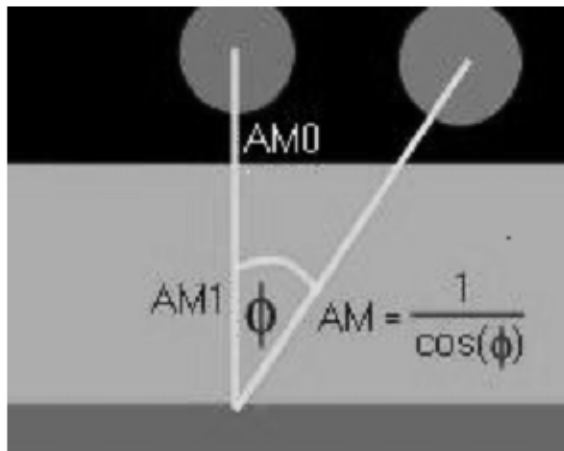
- ✧ 20000 lit of water
  - ✧ 3.3 tones of coal from being burned
  - ✧ 300 kg of ash from being disposed of landfills
  - ✧ 30 kg of SO<sub>2</sub> and 25 kg of NO<sub>x</sub> from causing acid rain
  - ✧ 8.5 tones of CO<sub>2</sub> from enhancing the greenhouse effect
-

# 태양전지의 역사

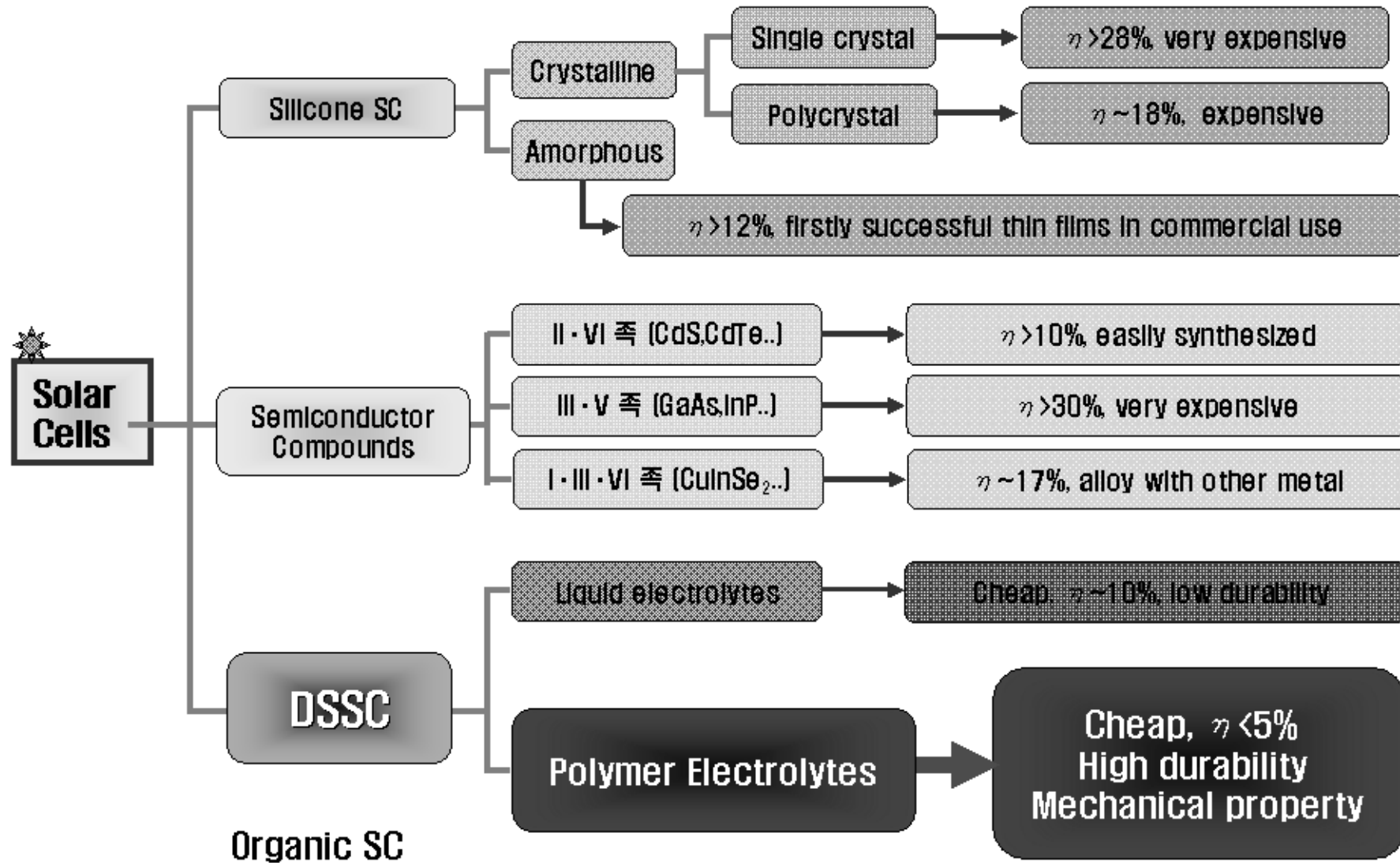
연 대	특 징
1839 년	E. Becquerel, Photovoltaic (PV) effect 발견
1883 년	C. Fritts, 최초의 Se 태양전지 제작
1930 년	L. Grohndahl, $Cu_2O/Cu$ 태양전지 연구
1941 년	R. Ohl, Si 태양전지 연구
1950 년대	반도체 기술 발전
1954 년	Bell Lab., 결정질 Si 태양전지 (효율 4%) 개발성공
1958 년	미국 우주선(Vanguard I) 보조전원 사용 (5 mW), 태양광 산업 태동
1970 년대	석유파동으로 지상용 전원으로 활용모색
1974 년	일본, 선샤인 계획 시작
1980 년대	태양전지 개발 본격화, 신재료 개발 (CdTe, $CuInSe_2$ , $TiO_2$ 등)
1991 년	M. Grätzel, 고효율 저가 광감응 염료 태양전지 발표 (Nature)
1999 년	환경친화적 발전기술로 부각, 전세계 연간 생산량 200MWp
2001 년	De Pauli, 고분자 전해질 염료감응 태양전지 최초 발표 (Adv. Mater.)

# Terminology

- Photovoltaic : light + Alessandro Volta = light electricity
- Air Mass (AM)
  - degree of light decrease by absorption, reflection, refraction
  - AM0: outside atmosphere  $\sim 1367 \text{ W/m}^2$  (136.7  $\text{mW/cm}^2$ )
  - AM  $\alpha = 1/\cos\phi$ ; angle from the horizon
  - AM1 : at  $\phi = 48.2^\circ \sim \text{one sun}$  (1000  $\text{W/m}^2$ )



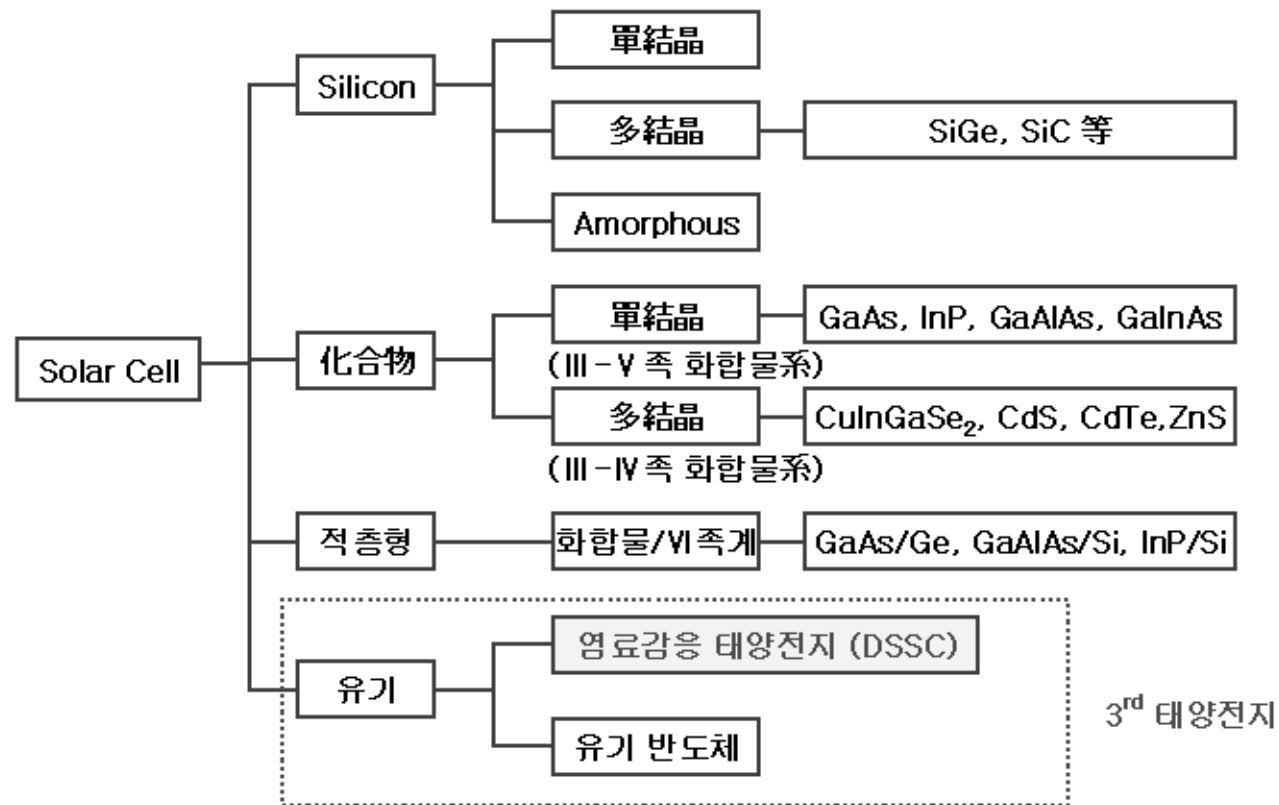
# Types of Solar Cells



# Generation of Solar Cells

## Photovoltaics: from physics to nature

- 1<sup>st</sup> Generation: Silicon crystalline
- 2<sup>nd</sup> : Silicon amorphous, thin films
- 3<sup>rd</sup> : Nanotechnology & Biomimetics
- 4<sup>th</sup> : Biological



# 태양전지 비교

## 반도체 태양전지

### 장 점

- ※ 고효율 (30% 이상) 태양전지 제조 가능

### 단 점

- ※ 고효율 태양전지 제조 시 원료비용 및 제조비용 부담이 매우 큼
- ※ 고순도를 요하는 공정이므로 제조공정이 복잡하고 어려움
- ※ 환경에 유해한 물질 발생

## 광감응 염료 태양전지

### 장 점

- ※ 기존 비정질 실리콘 태양전지에 버금가는 에너지변환 효율 (습식 태양전지)
- ※ 제조단가는 실리콘 태양전지의 5분의 1 수준
- ※ 환경친화적 제조공정

### 단 점

- ※ 습식 태양전지의 경우, 용매의 휘발 및 누출에 따른 내구성 저하 문제



# Trends in Industry

## DSSC Manufacturers

Konarka, MA



INAP, Gelsenkirchen, Germany

ECN, Petten, Netherlands

Solaronix, Aubonne, Swiss

IMRA-Europe, France

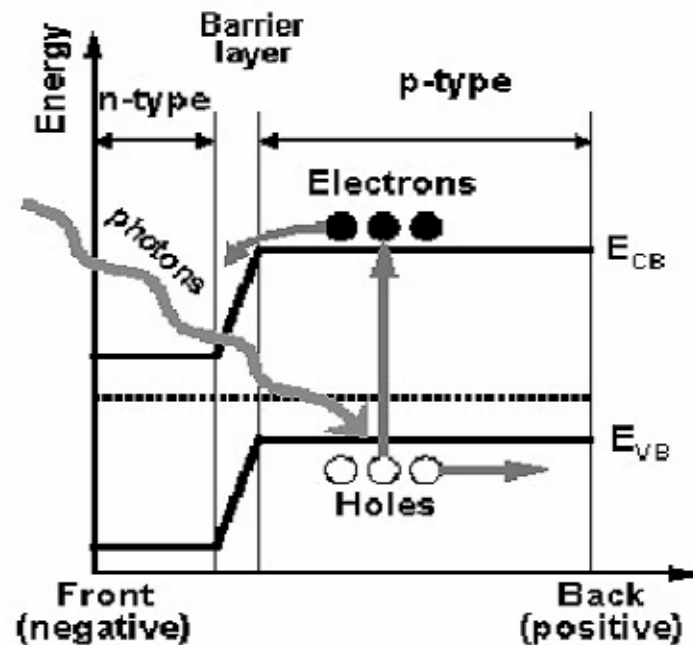
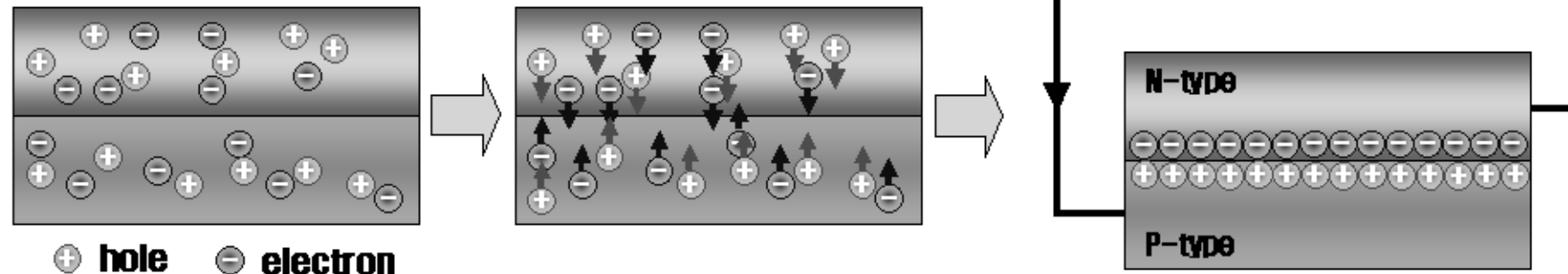


**Japan  
50 companies**

STI, AU

# Principles of Inorganic Solar Cells

## ☼ *Semi-conductor (p-n junction) SC*



N type: e<sup>-</sup> transfer, e<sup>-</sup> acceptor

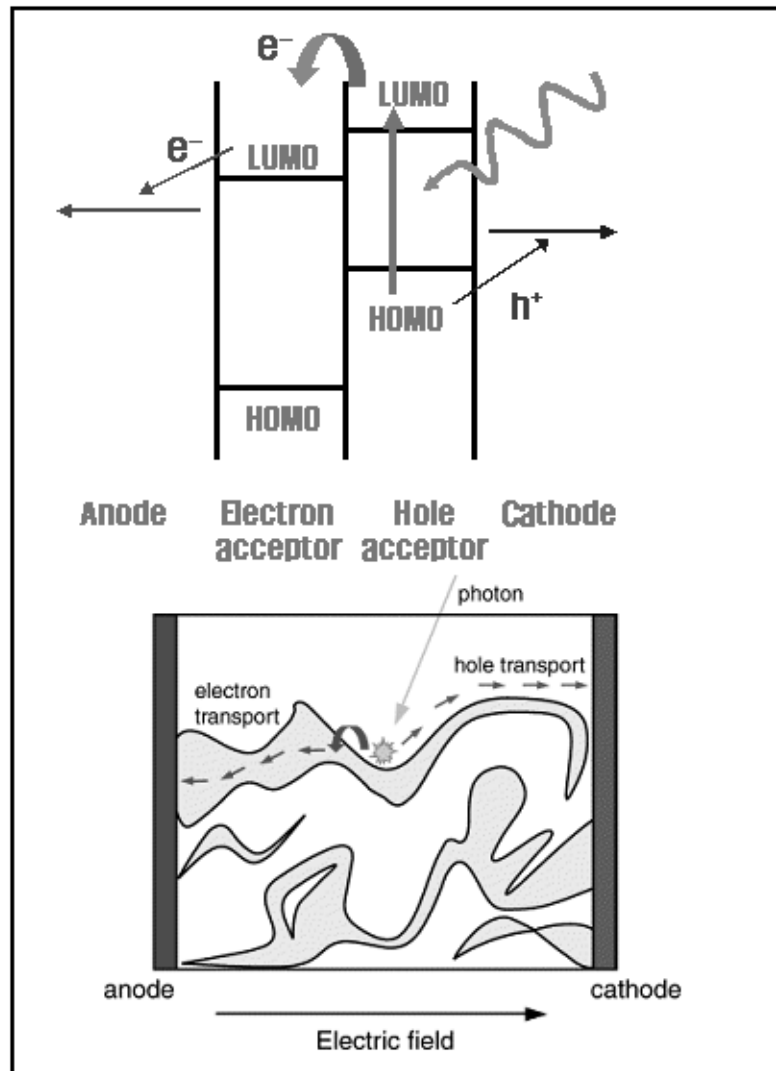
P type: hole transfer, e<sup>-</sup> donor

Band gap  $E = E_{CB} - E_{VB}$   
 Photon with high  $E > E_{BG}$

CB: conduction band, 전도띠

VB: valence band, 가전도띠

# Organic Solar Cells



- Organic molecules
- D-A heterojunction
- dispersed heterojunction

Acceptor	Donor
Fullerene	Conducting P
Conducting P	Conducting P
Nano-inorganics	Conducting P

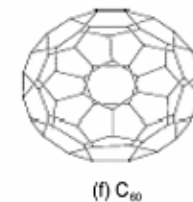
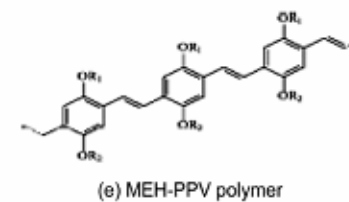
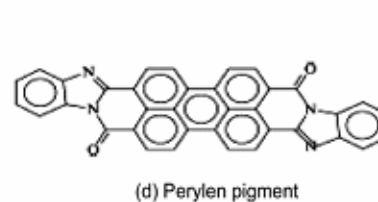
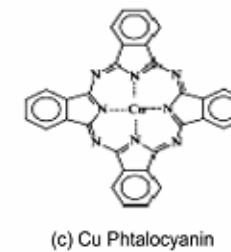
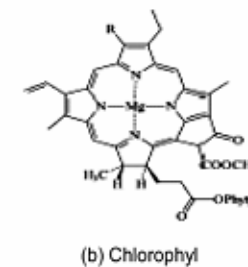
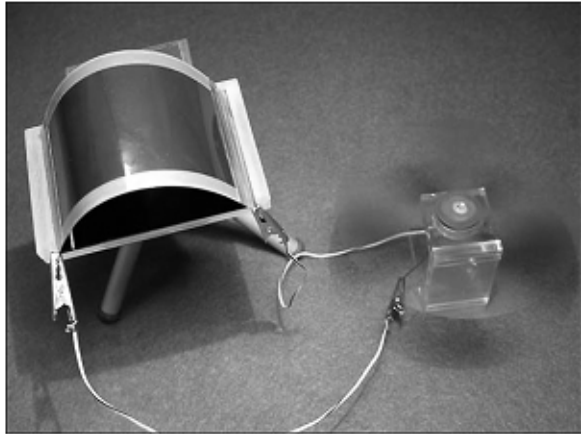


Fig. 13. Materials for organic solar cells: (a)-(c); donors, (d)-(e); acceptors.

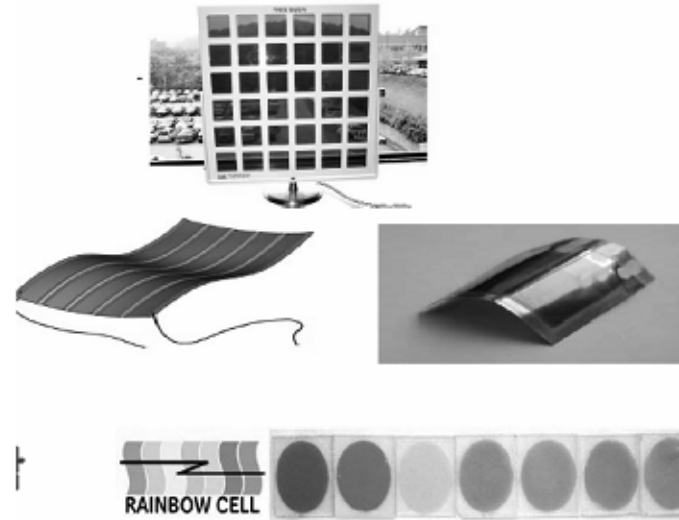
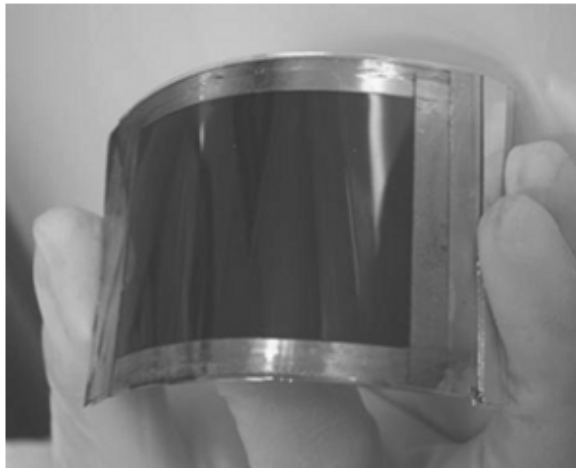


# Organic Solar Cells

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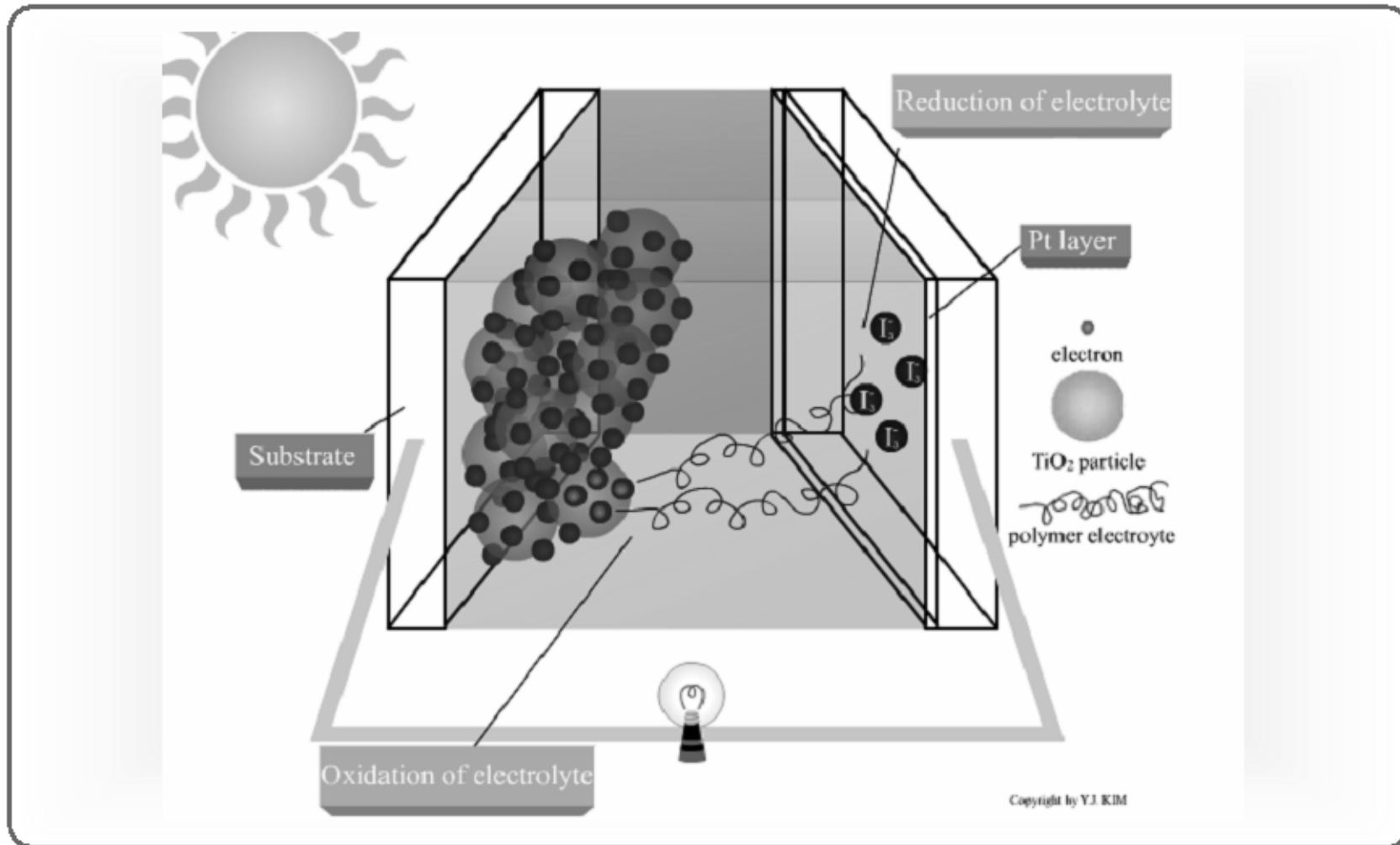


- **Organic Solar Cells**
  - Cheap, efficient
  - Improved stability
  - Transparent, flexible, colorful



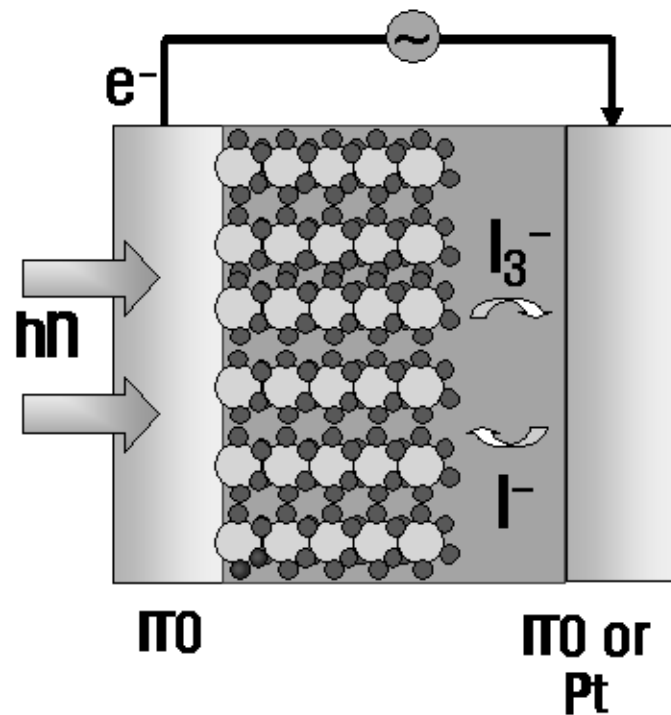
# Principles of Solar Cells

## ★ *Dye-Sensitized Solar Cells (DSSC)*



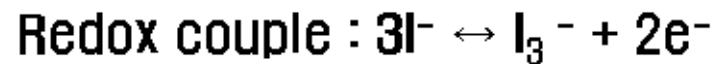
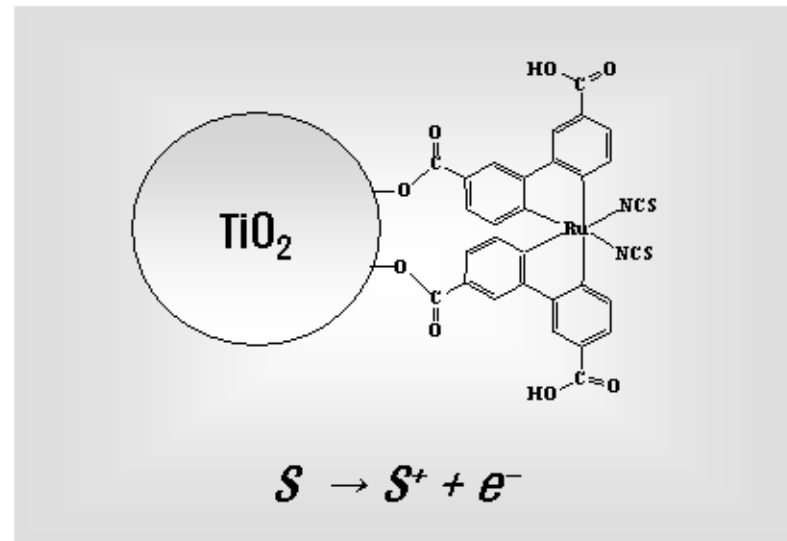
# Principles of Solar Cells

## ☼ *Dye-sensitized solar cells*



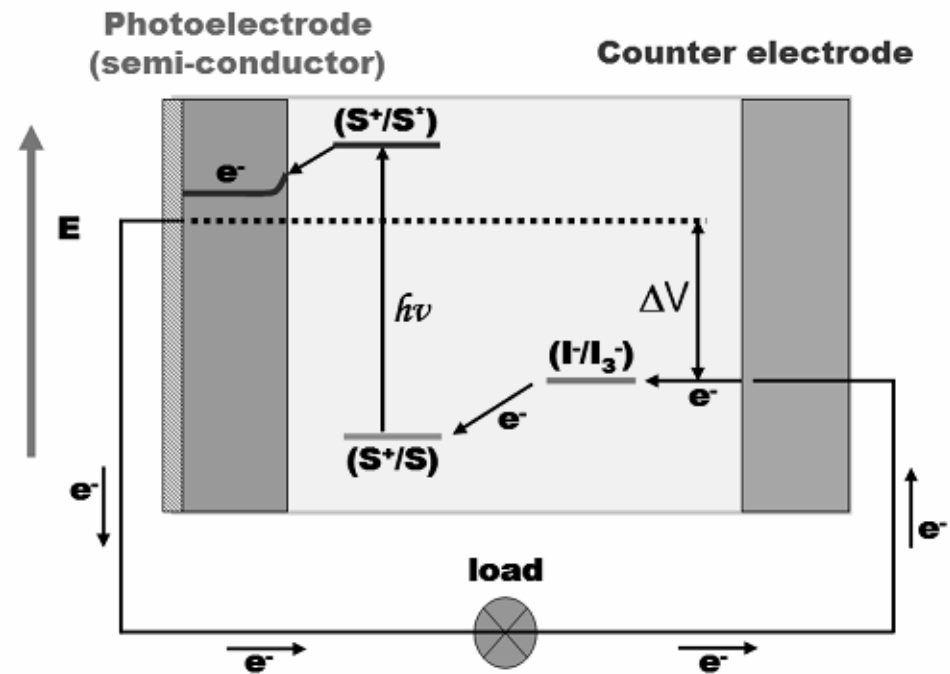
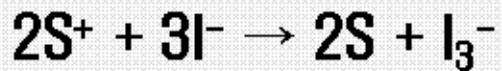
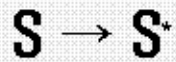
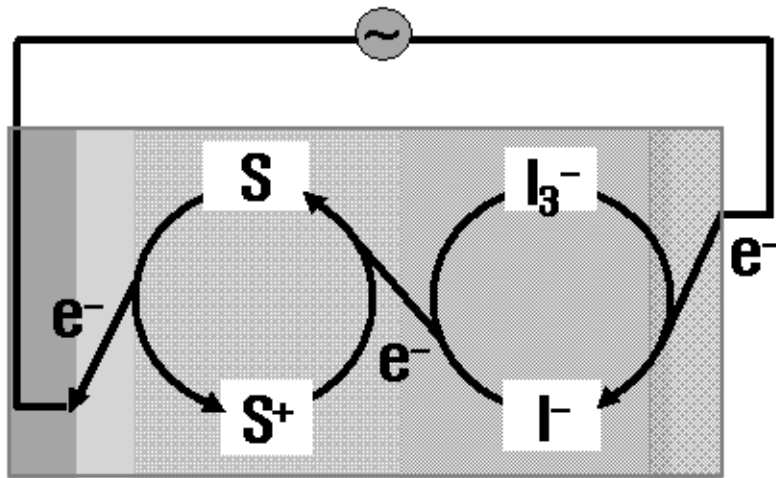
- : dye
- : semiconductor
- : electrolyte

## Ru Dye (sensitizer)/TiO<sub>2</sub>



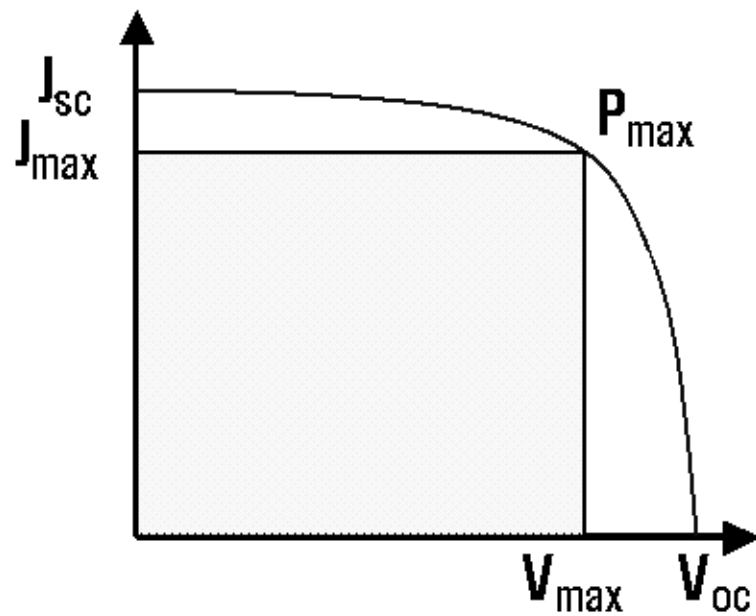
# Principles of Solar Cells

## ☼ *Dye-sensitized solar cells (DSSC)*



# Performance of Solar Cells

## ☀ Typical J–V curve of solar cell



$$FF = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}}$$



$$\begin{aligned} \eta(\%) &= \frac{V_{max} \cdot J_{max}}{P_{in}} \times 100 \\ &= \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100 \end{aligned}$$

### ☞ Solar cell performance

- $V_{oc}$  : Open-Circuit Voltage,       $J_{sc}$  : Short-Circuit Current
- $FF$  : Fill Factor,                       $\eta$  : Overall Conversion Efficiency



# Characteristics of DSSC

– promising candidates for renewable clean energy source

Low Costs : 1/3 ~1/5 of conventional Si S/C

Green Technology: non-toxic mater.

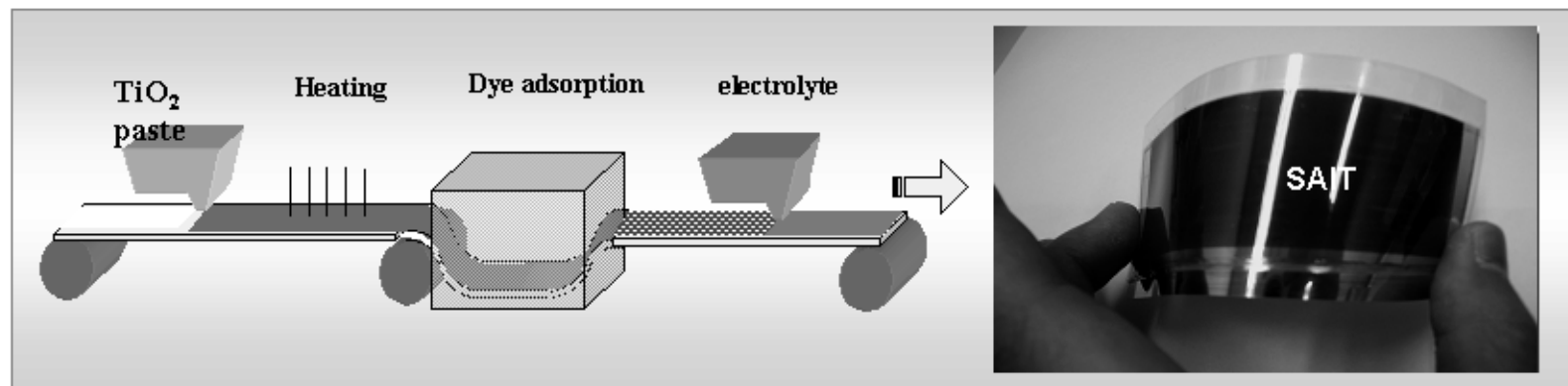
Transparent: Power window, smart window

Coloration: Rainbow cell

Flexibility: Flexible Battery & Device



TOYOTA-AISIN精機

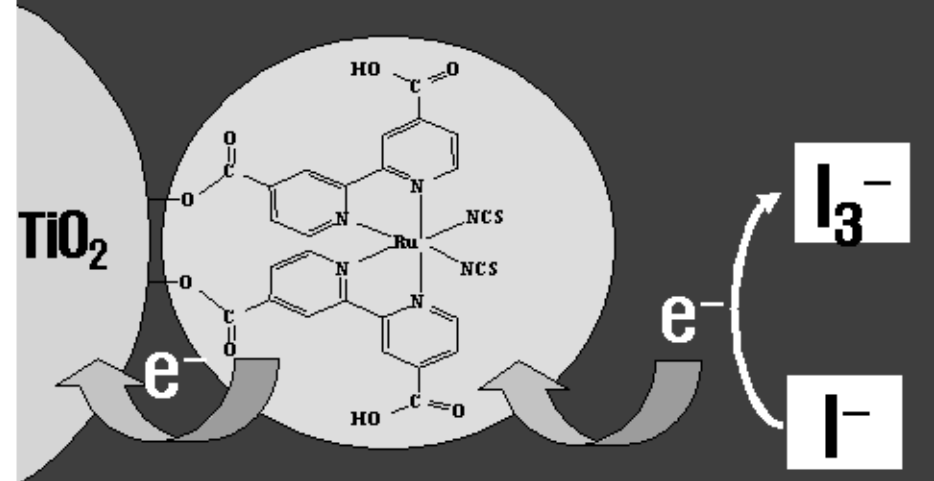


# Roles of Electrolytes

## Electrolytes:

- $I^-$  and  $I_3^-$  conductor
- interfacial contactor for dye
- electron barrier or hole conductor
- electrochemical reaction media
- mechanical separator

## Contact of electrolyte with dyes:



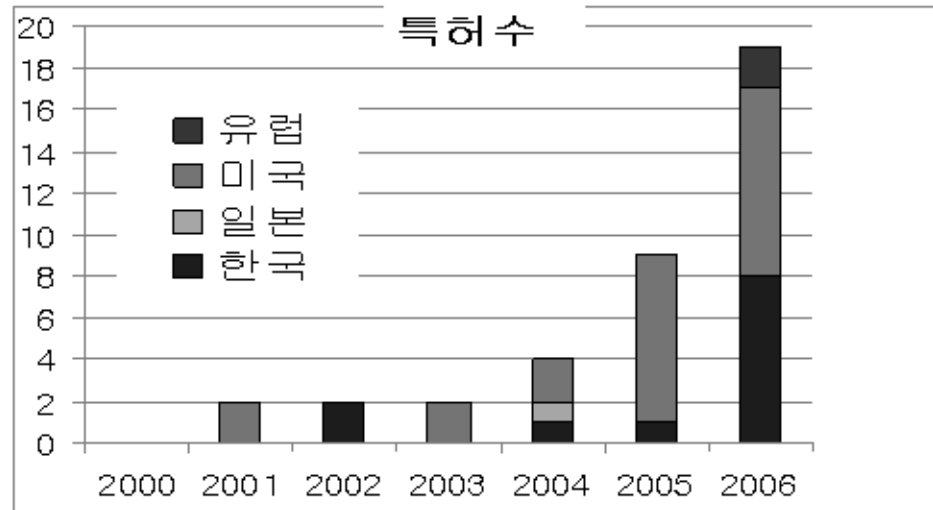
# Why Polymer Electrolyte DSSC ?

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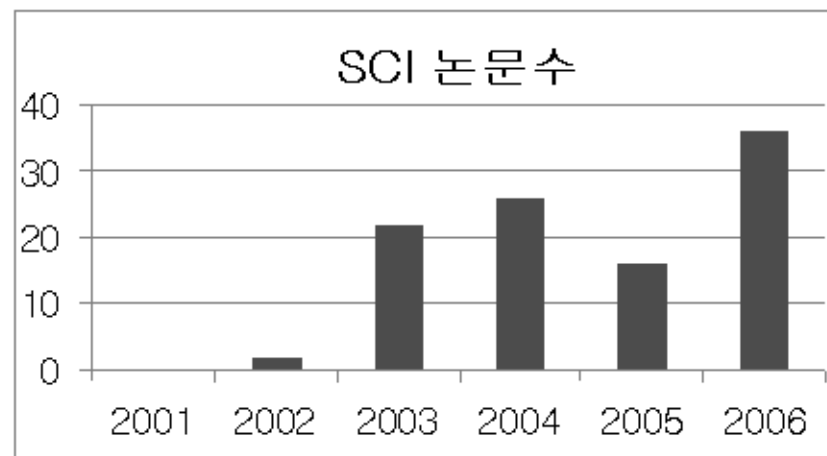
- ✦ **Cheap (1/5 of Silicone solar cell)  
Environmentally friend.**
  - ✦ **Thin, Flexible, light**
  - ✦ **Higher durability using solid or gel type solar cell**
  - ✦ **World-wide great attention very recently**
-

# Research Trends in PE-SC

## ☀ WIPS Patent



## ☀ Web of Science SCI Paper





**Break ???**

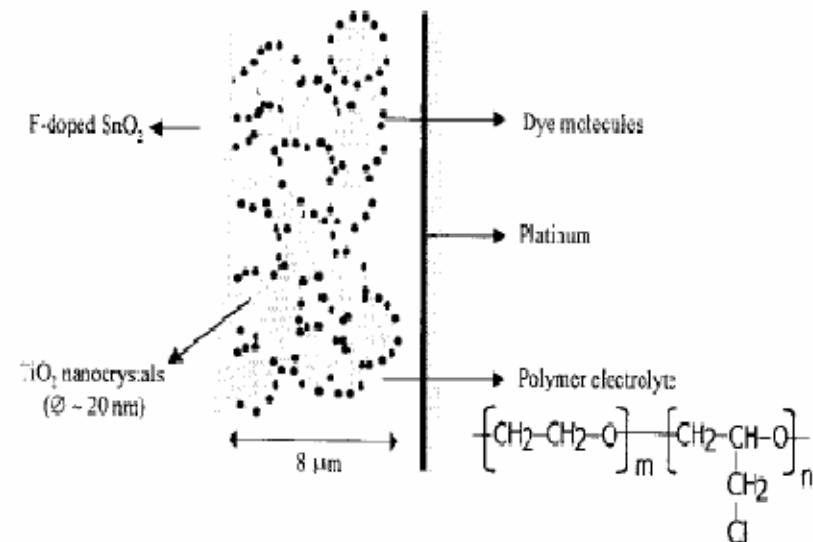
# Polymer Electrolytes Review – 1

- Title: Dye-sensitized nanocrystalline solar cells employing a polymer electrolyte
- Authors: De Paoli et al. (Brazil)
- *Adv. Mater.* 2001, 13, 826.

## HIGHLIGHTS

👉 *Epychlomer(1.3M)/NaI/I<sub>2</sub>*

- *High efficiency*  
: 2.6 % at 10mW/cm<sup>2</sup>
- *Successful penetration*  
– due to nature and viscosity of polymer electrolytes



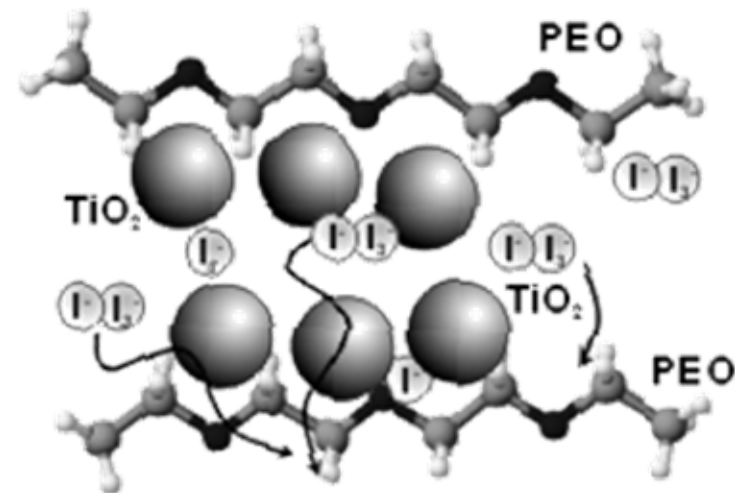
# Polymer Electrolytes Review – 2

- Title: Binary polyethylene oxide/titania solid-state redox electrolyte for highly efficient nanocrystalline TiO<sub>2</sub> photoelectrochemical cells
- Authors: Stergiopoulos, T. et al (Greece)
- *Nano Letter*, 2002, 2, 1259.

## HIGHLIGHTS

☞ ***PEO(2M)/TiO<sub>2</sub>/LiI/I<sub>2</sub>***

- *Reduced crystallinity*
- *Enhanced the mobility of I<sup>-</sup>/I<sub>3</sub><sup>-</sup>*
- *outstanding efficiency (4.2%)*



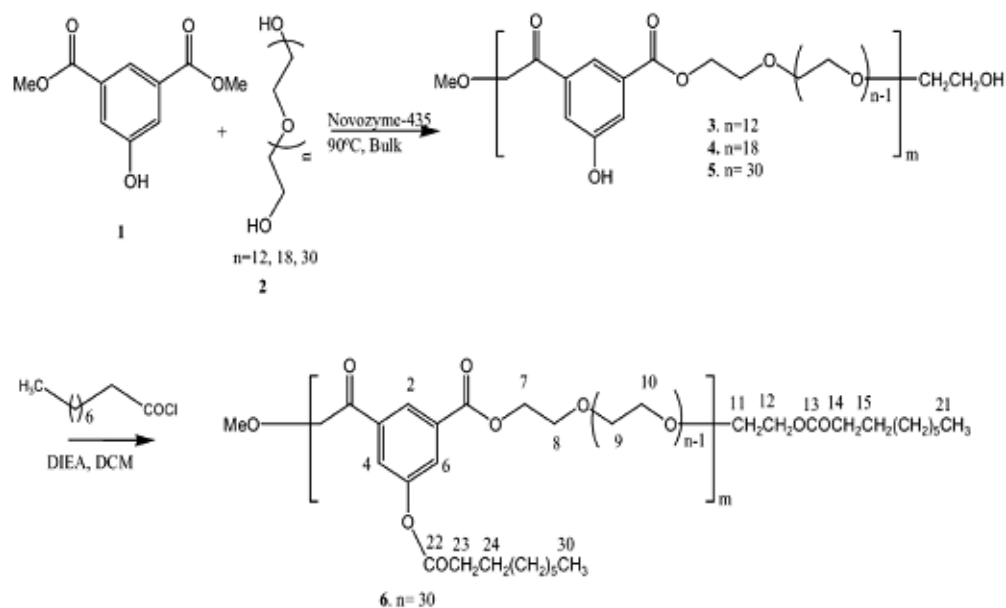
# Polymer Electrolytes Review – 3

- Title: Flexible, Dye-Sensitized Nanocrystalline Solar Cells Employing Biocatalytically Synthesized Polymeric Electrolytes
- Author: Rajesh Kumar et al. (University of Massachusetts)
- *Chem. Mater.* 2004, 16, 4841.

## HIGHLIGHTS

### PEGylated polymers

- *Biocatalytic approach*  
– *Novozyme catalyzed reaction*
- *outstanding efficiency (4.6%)*





# Other Polymer Electrolytes

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[1] Y. Ren et al. "Application of PEO based gel network polymer electrolytes in dye-sensitized photoelectrochemical cells", *Solar Energy Materials Solar Cells*, 2002, 71, 253.

[2] O. A. Ileperuma, "Dye-sensitised photoelectrochemical solar cells with polyacrylonitrile based solid polymer electrolytes", *Electrochimica Acta*, 2002, 47, 2801.

[3] J. Kang, "Polymer electrolytes from PEO and novel quaternary ammonium iodides for dye-sensitized solar cells", *Electrochimica Acta*, 2003, 48, 2487.

[4] G. Wang, "Gel polymer electrolytes based on polyacrylonitrile and a novel quaternary ammonium salt for dye-sensitized solar cells", *Materials Research Bulletin*, 2004, 39, 2113.

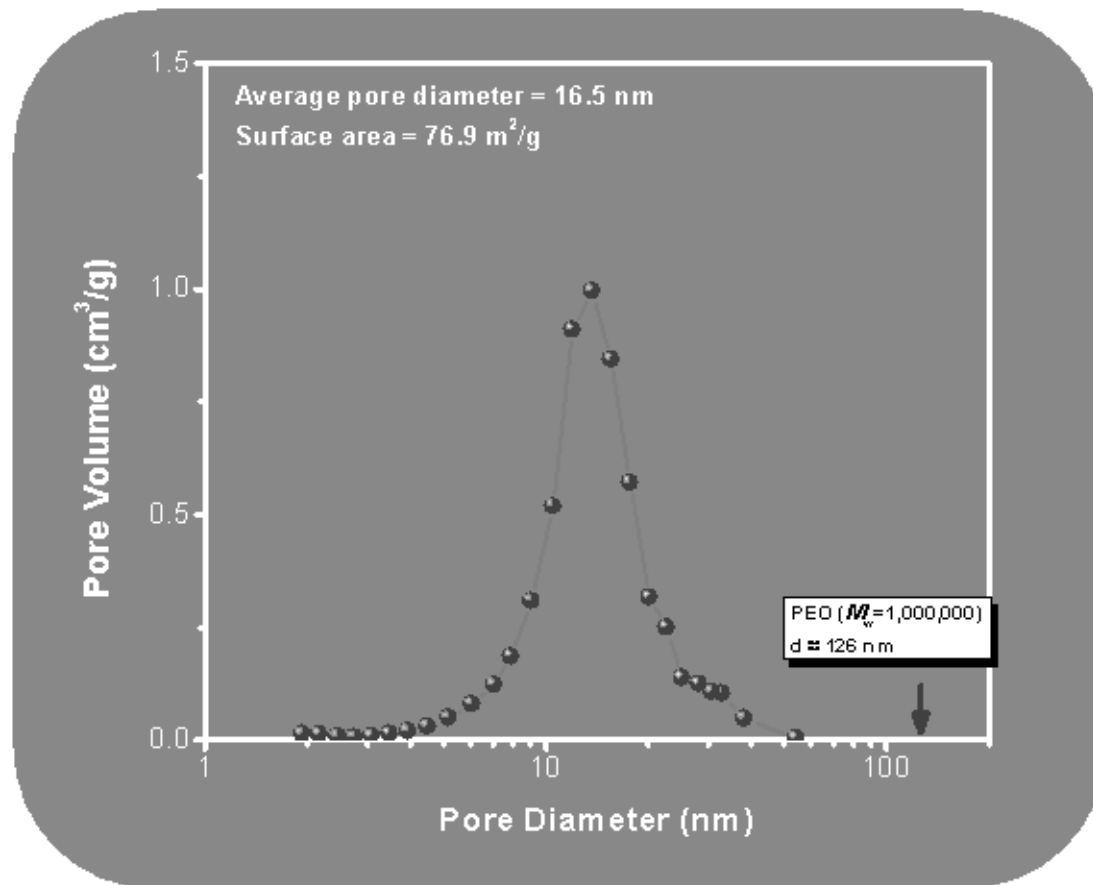
[5] W. Li, "A novel polymer quaternary ammonium iodide and application in quasi-solid-state dye-sensitized solar cells", *J. Photochem. Photobiol. A: Chem.* 2005, 170, 1.

[6] J. Wu, "Gel polymer electrolyte based on poly(acrylonitrile-co-styrene) and a novel organic iodide salt for quasi-solid state dye-sensitized solar cell", *Electrochimica Acta*, 2006, 51, 4243.

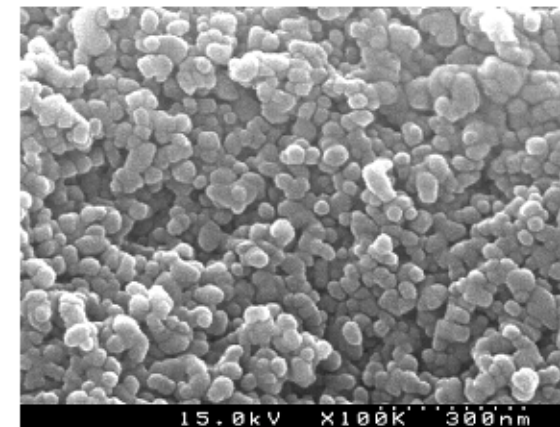
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# Why Low Efficiency ?

## Pore Size Distribution – BET



FE-SEM image of TiO<sub>2</sub> electrode

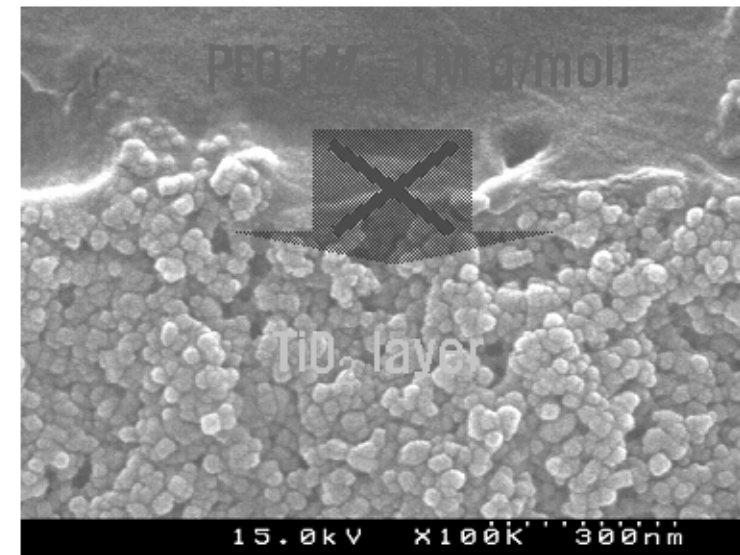


# Why Low Efficiency ?

$$R_g = c \cdot M_w^{0.5 \pm 0.1} \quad (\text{nm})$$

- Poly(ethylene oxide) (PEO)  
 $c=0.063$  (in diluted solution)  
 $c=0.042$  (in molten state)

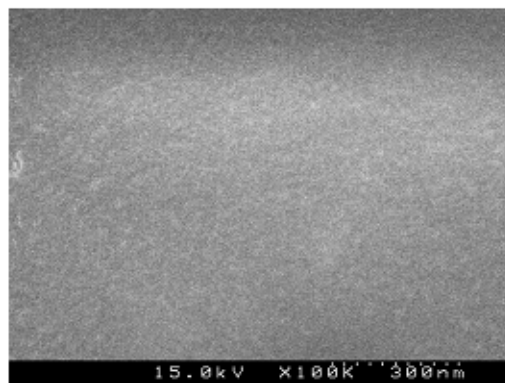
- *Example: PEO (Mw=1,000,000)*  
 $R_g = 63 \text{ nm}$  (in diluted solution)  
 $R_g = 42 \text{ nm}$  (in molten state)



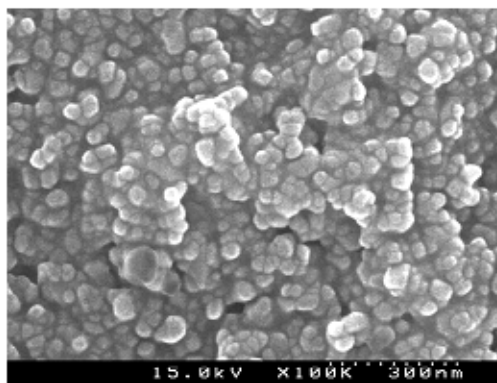
>  $\text{TiO}_2$  pore size  
[~16.5 nm]

- Poor penetration
- Low conductivity

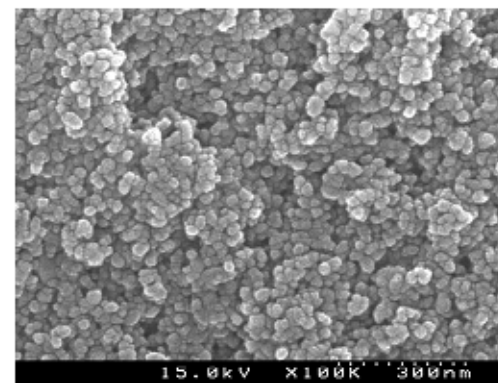
# FE-SEM images – Size balance



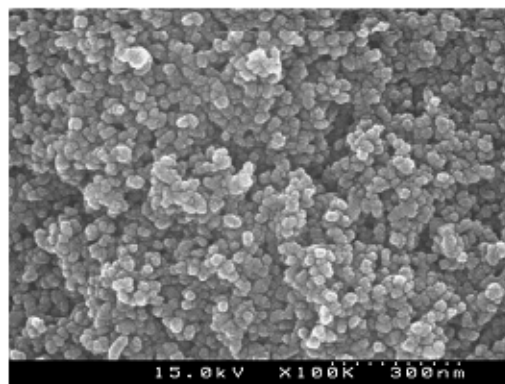
$M_w=1K$   
( $R_g=2.0$  nm)



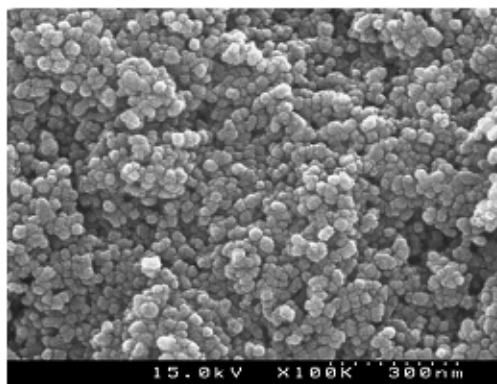
$M_w=4.6K$   
( $R_g=4.3$  nm)



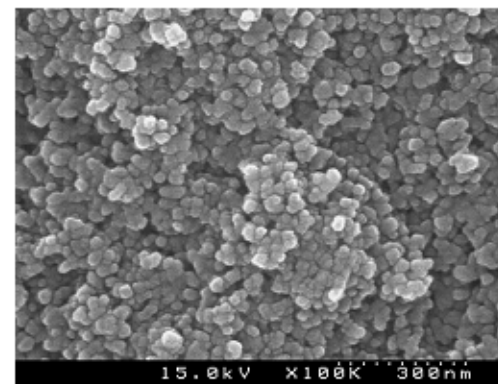
$M_w=8K$   
( $R_g=5.6$  nm)



$M_w=10K$   
( $R_g=6.3$  nm)



$M_w=100K$   
( $R_g=19.9$  nm)

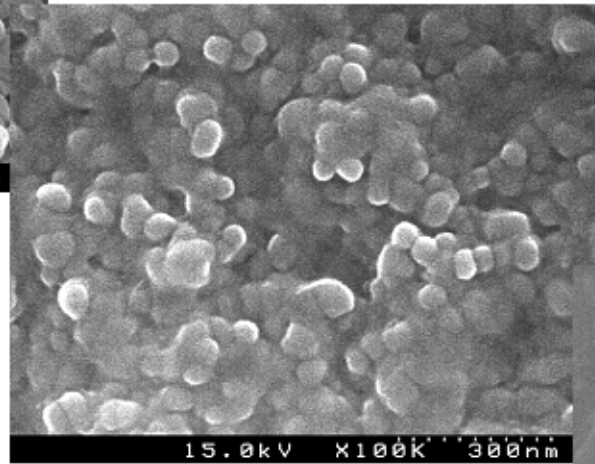


$M_w=600K$   
( $R_g=48.8$  nm)

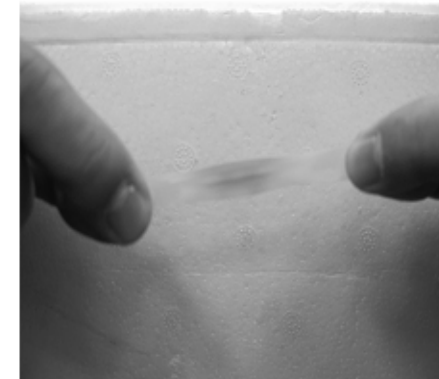
# Size balance vs. Efficiency



$\eta = 0.01\%$



$\eta = 1.25\%$



$\eta = 3.84\%$

## Low Mw PEs

- better penetration
- high conductivity
- poor mechanical property

# Oligomer Approach

Prof. Kang at Hanyang Univ. /  
Prof. Kim at Yonsei Univ.

- *Oligomer :  $M_w \sim 1000$ , liquid ( $R_g < 3 \text{ nm}$ )*
- *To enlarge the interfacial contact area between dyes and electrolyte*
- *To improve the ionic conductivity*

during preparation  
(liquid oligomer )

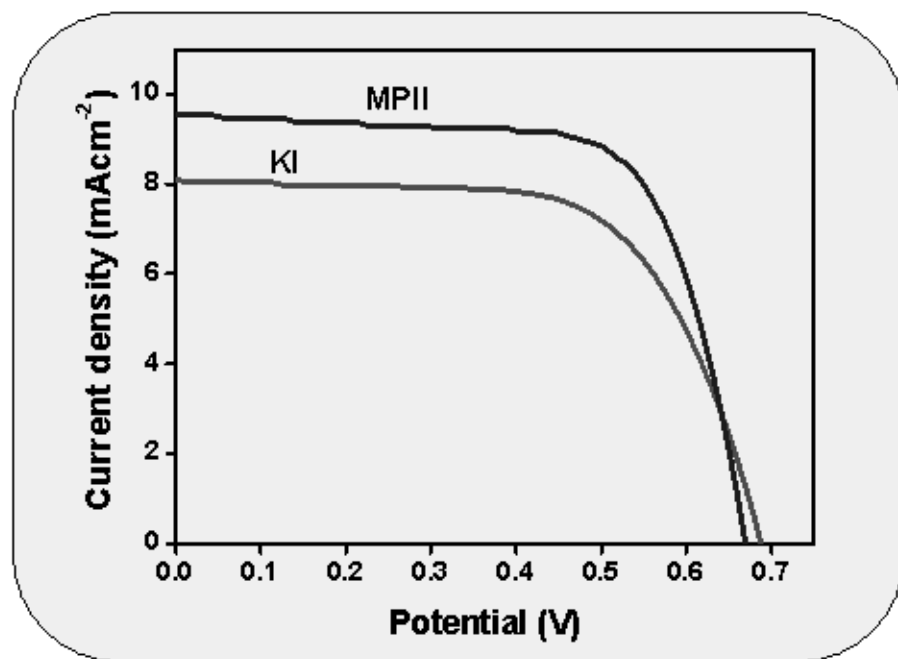


after preparation  
(solid polymer )

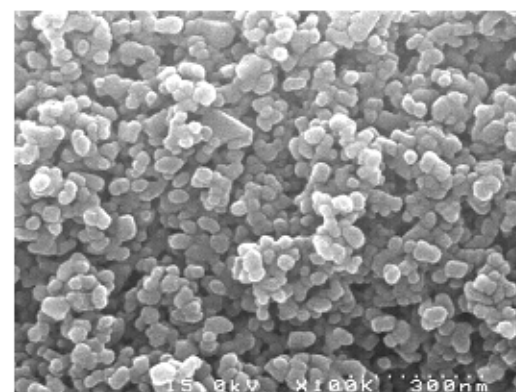
*in situ* solidification  
during solvent evaporation

# HB Polymer Electrolytes

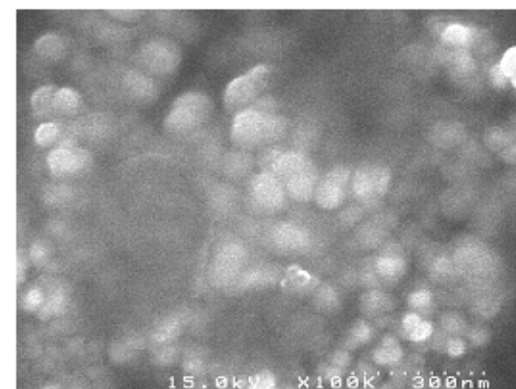
## *PEO + Silica Nanoparticles*



*Efficiency 4.5%*  
*Fill factor 70.0%*  
*at 100 mW/cm<sup>2</sup>*



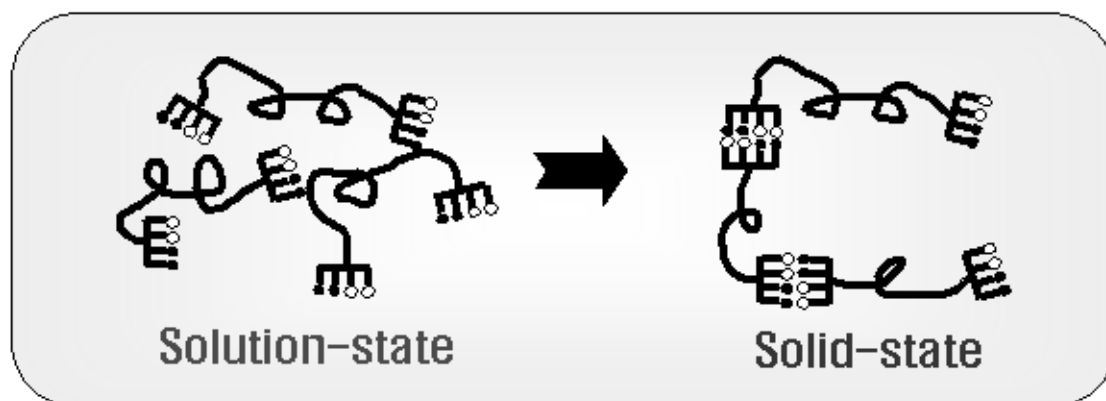
(a) Bare TiO<sub>2</sub> layers



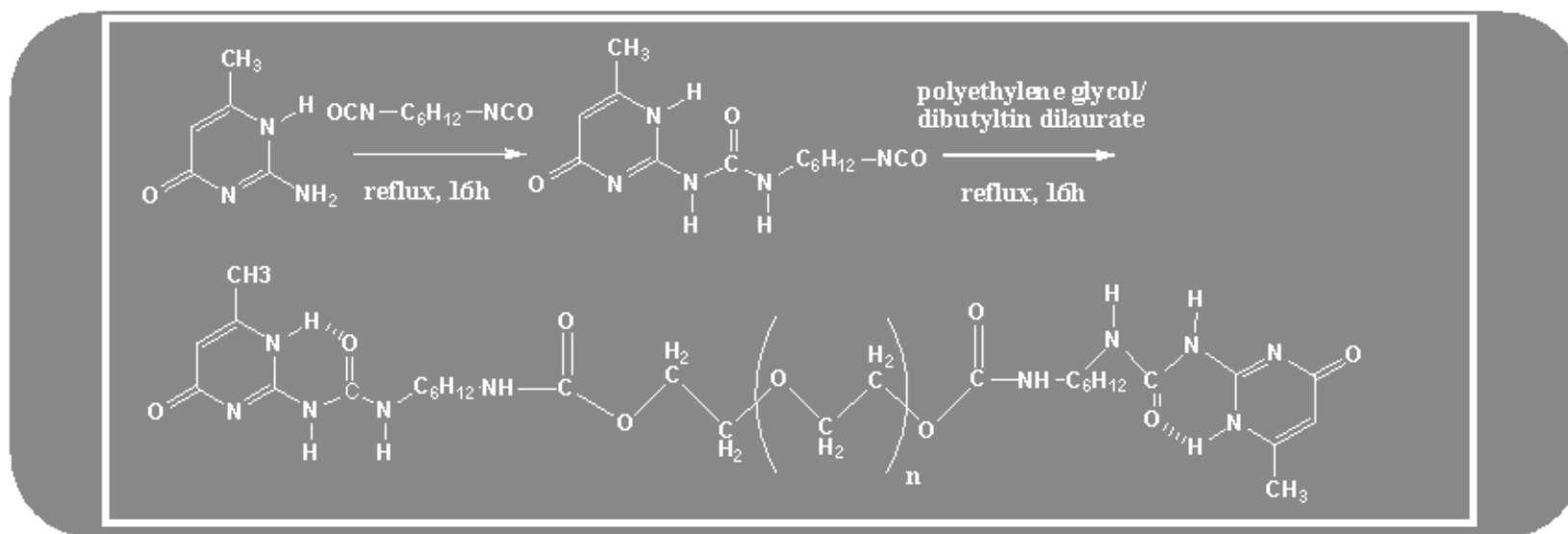
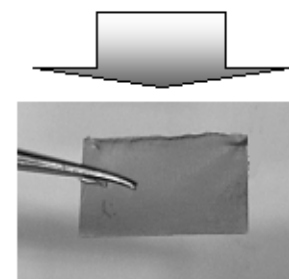
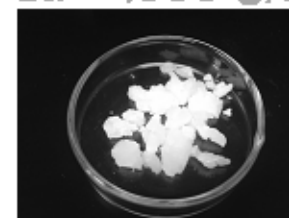
(b) TiO<sub>2</sub> with PEs

# Quadruple HB Polymer (QHBP)

## Design of Electrolytes



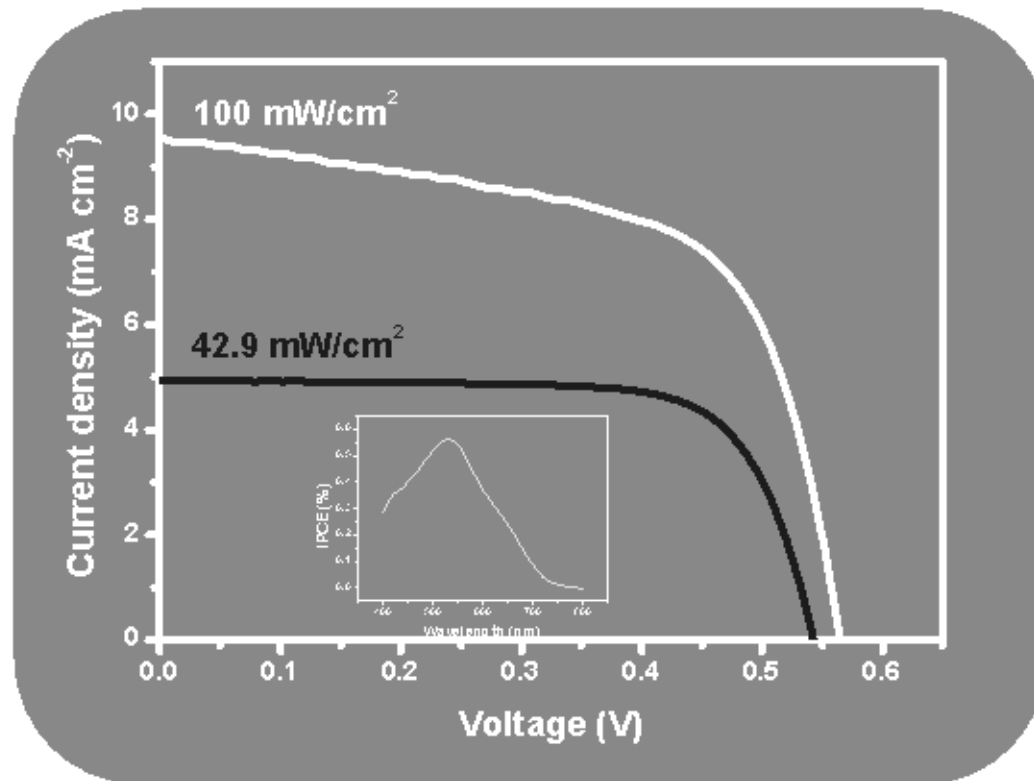
PEG: 1,000 g/mol





# Cell Performance

## Energy Conversion Efficiency



$$V_{OC} : 0.57 \text{ V}$$

$$J_{SC} : 9.53 \text{ mA/cm}^2$$

$$FF : 62 \%$$

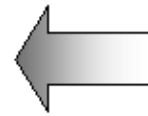
$$\eta : \underline{3.34 \%} \text{ [4.6\% at } 42.9 \text{ mW/cm}^2\text{]}$$

$$P_{in} : 100 \text{ mW/cm}^2$$

***J-V* curves of DSSCs using QHBP/MPII electrolyte**

# Solid State DSSC

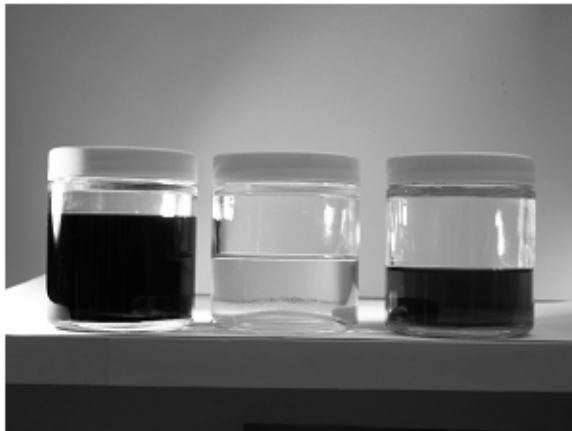
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**Power window**



**Large area (20x20 cm<sup>2</sup>)**



**dyes**



# Results about Solar Cells



## Solid organic solar cell

2.6 % at 0.1 sun and 1.6 % at 1 sun  
by de Pauli group: *Adv. Mater.* 2001, 13, 826

*Epychlomer/NaI/I<sub>2</sub>*

4.2 % at 0.65 sun

by Stergiopoulos group: *Nano Letters* 2002, 2, 1259

*PEO/TiO<sub>2</sub>/LiI/I<sub>2</sub>*

8.1 % at 0.1 sun  
4.5 % at 1 sun

The Highest values !!!!  
Prof. Kang at Hanyang Univ. /  
Prof. Kim at Yonsei Univ.

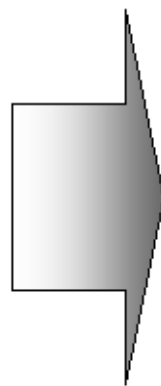
*Adv. Mater*, *Chem. Commun.* *J. Phys. Chem.*  
[2004, 2005, 2006]  
Press & Broadcasting [2004]

# One-step Synthesis

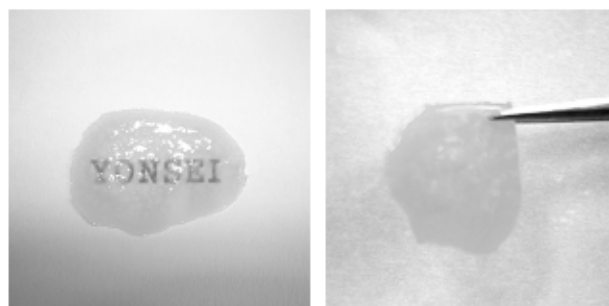
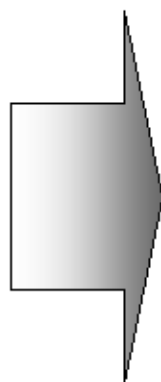
Prof. Kim at Yonsei Univ.



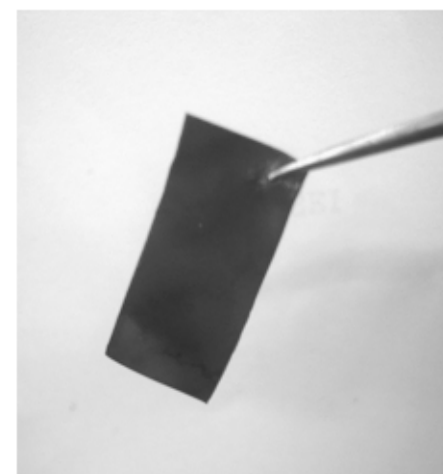
Pristine Polymer



QHBP



QHBP/KI



QHBP/KI/I<sub>2</sub>

# Recent Research Trends

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## 1. Nanocrystalline Oxides

Surface Modification  
Morphology Modification (nanorod...)  
Bilayer Structure  
TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>.....

## 2. Electrolytes

High Boiling Point & Low Viscous Sovent  
Polymer Electrolyte  
Solid State (including p-type conductors)  
Room Temp. Molten Salt

## 3. Dye Molecules

Modification of Ruthenium Complexes  
Organic Dye, Inorganic Dye  
Natural Products

## 4. Basic Researches

Electron Transport Mechanism  
IMPS, IMVS, EIS, Random Walk etc.



**Higher  
Efficiency !!**

# Current Issues

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1. Understanding electron dynamics in DSSCs
  2. Electrolyte evaporation and degradation
    - Quasi or solid state DSSCs
  3. New sensitizers (dye or quantum dot)
  4. Recombination in the oxide layer
    - Preparation of the second oxide layer for passivation
  5. Flexible DSSCs
  6. Increasing efficiency and performance
  7. Long-term performance
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