Recent Advances in Dye-Sensitized Solar Cells

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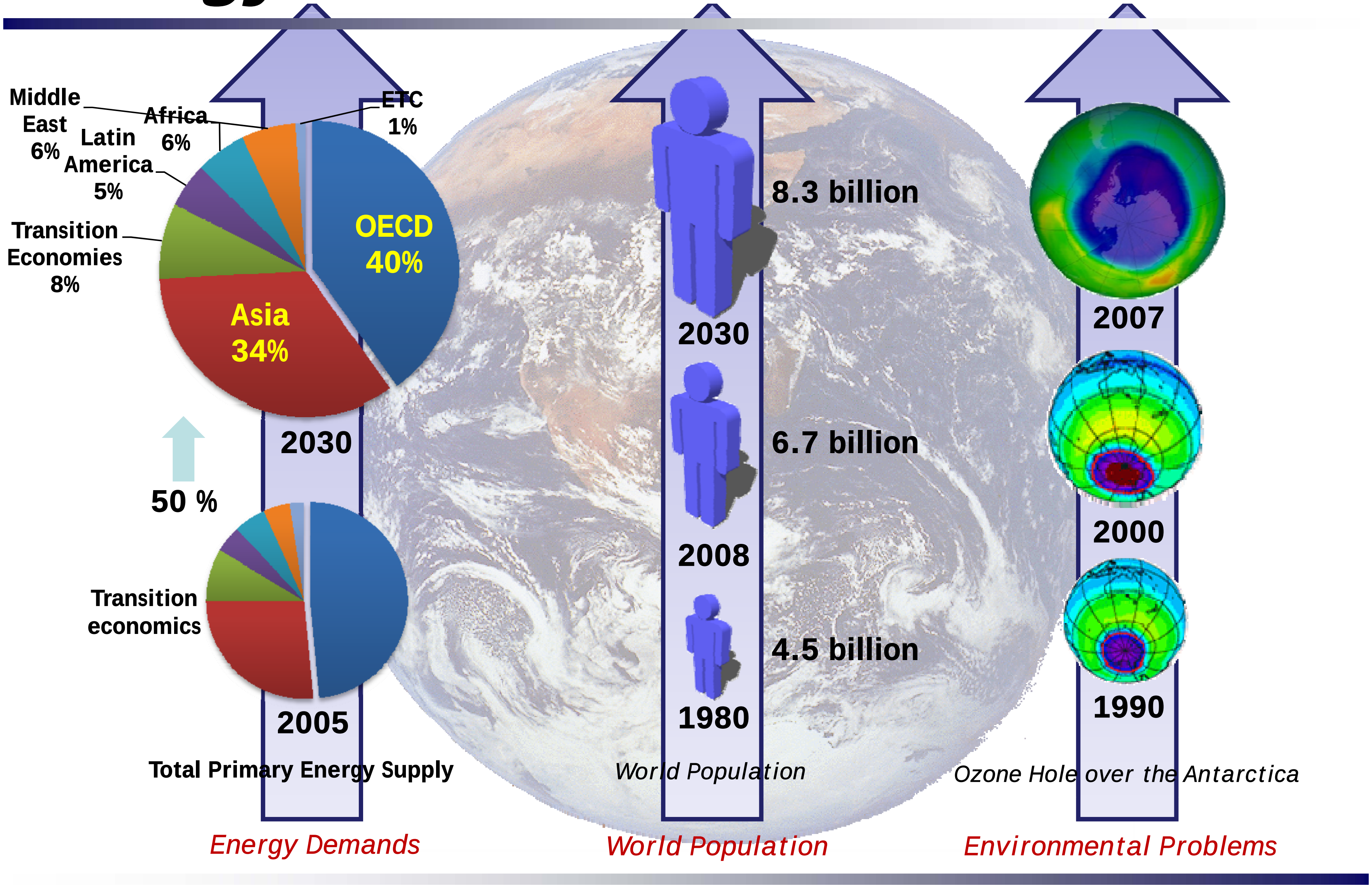
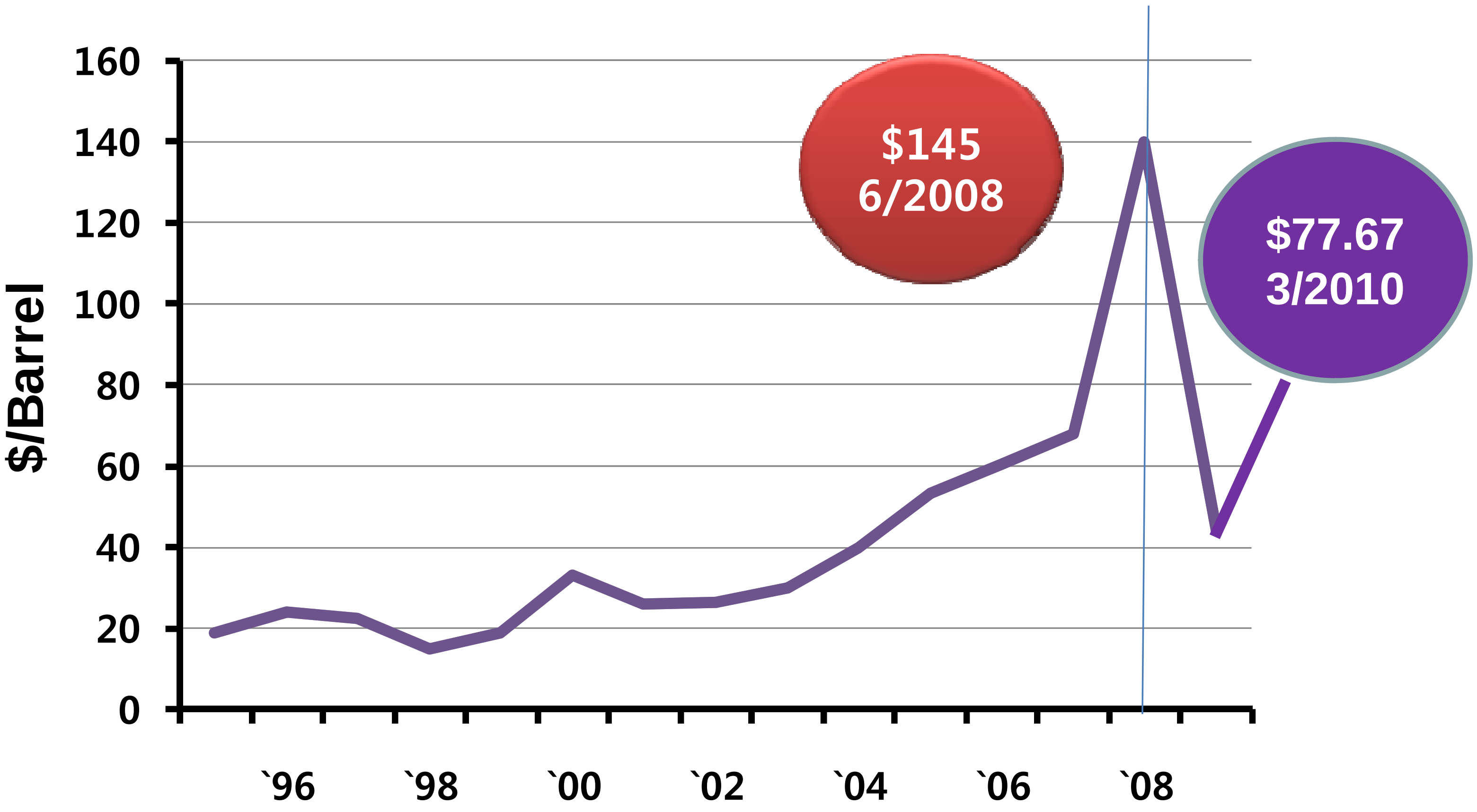
Energy Future

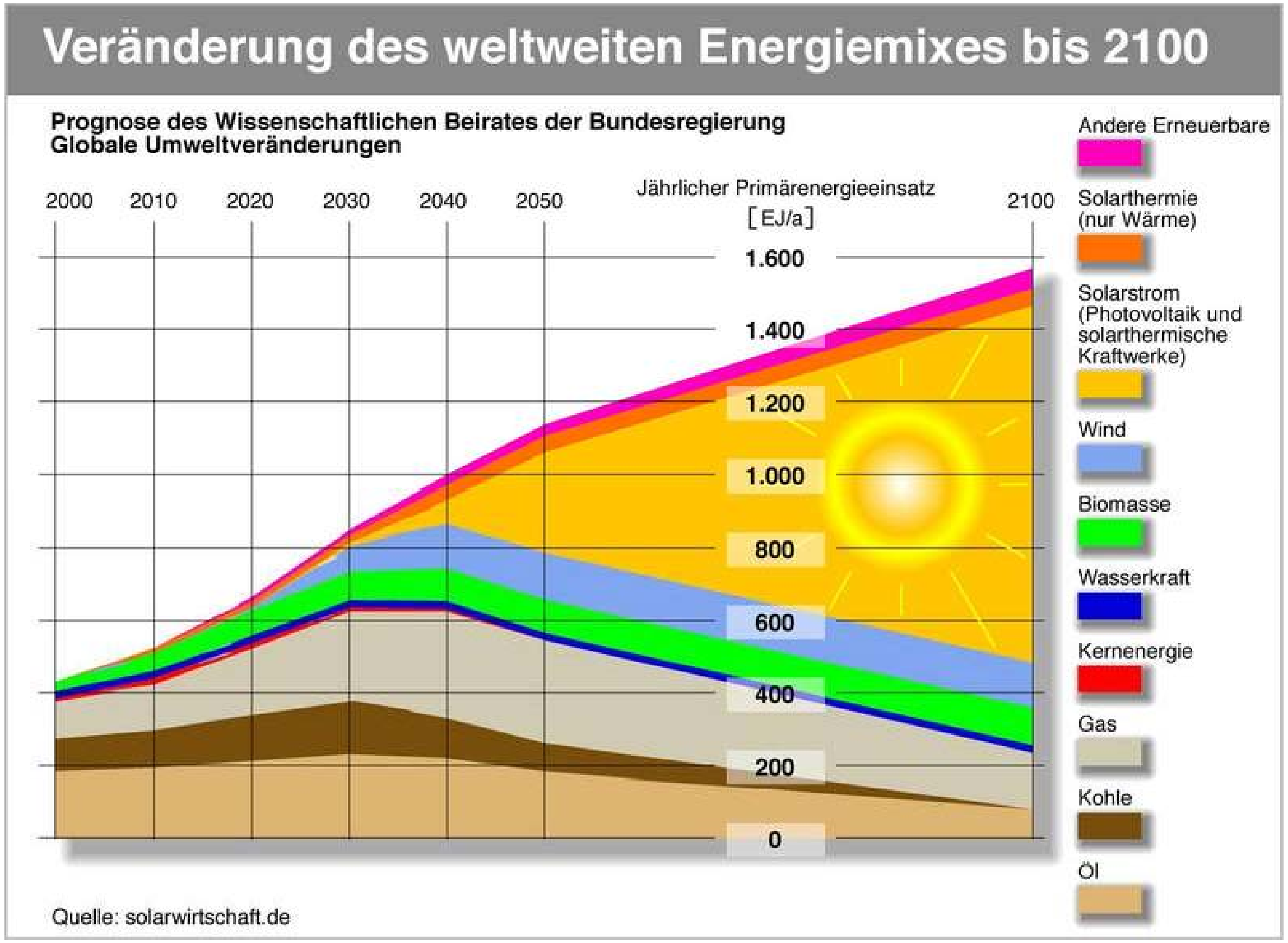


Change in Oil Price




News Focus
Officials at the U.S. Department of Energy are working to kindle support for a crash program to transform solar energy from a bit player into the world's leading power source
Is It Time to Shoot for the Sun?

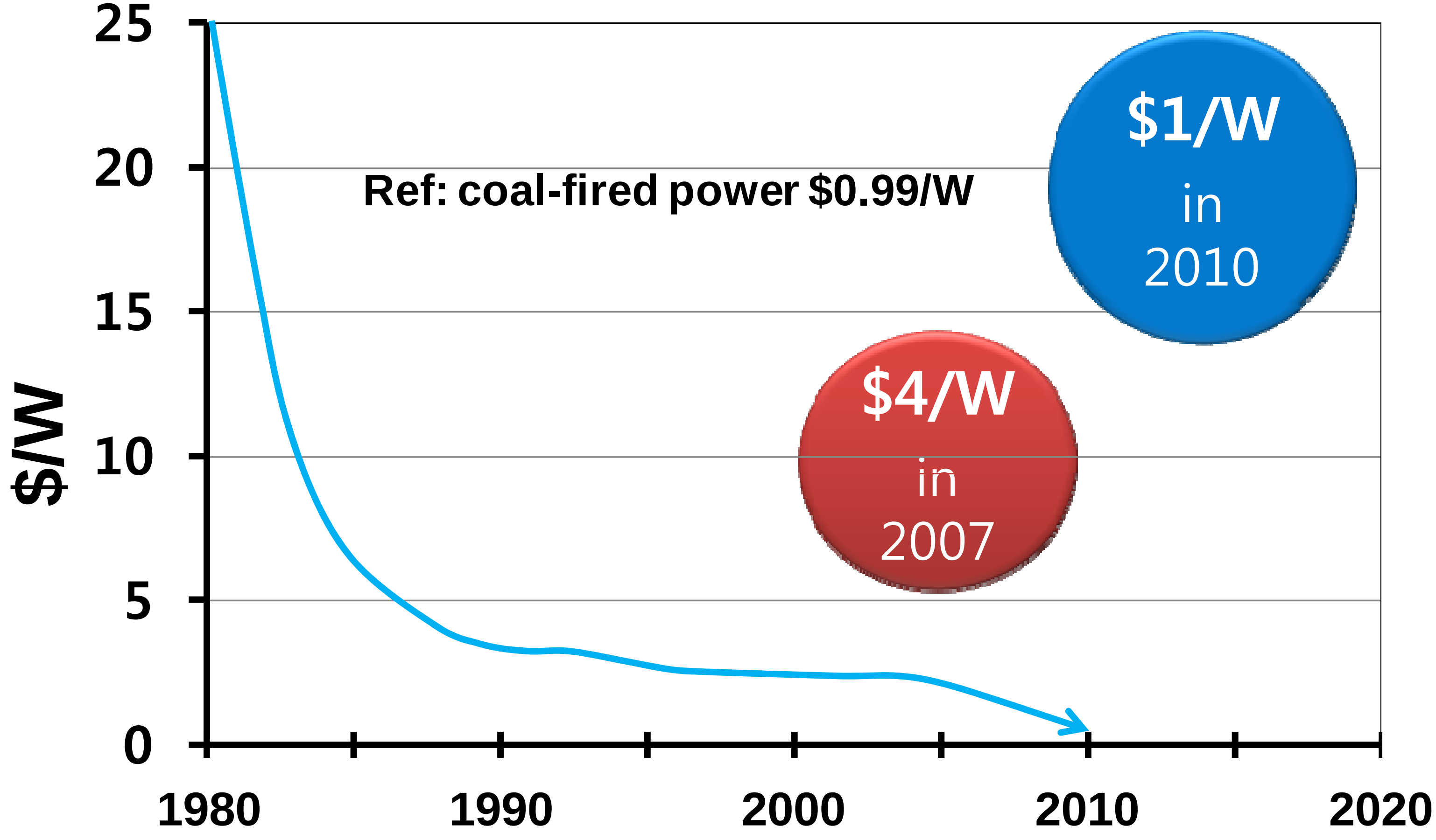
Future Market



Market share for solar cells will be almost 70 % of the total energy demands in 2100

(www.solarwirtsch.de).

Electricity Production Cost



Average cost per watt of PV module 1985-2010.
(Source: Earth Policy Institute, 2007)

Electricity Production Cost

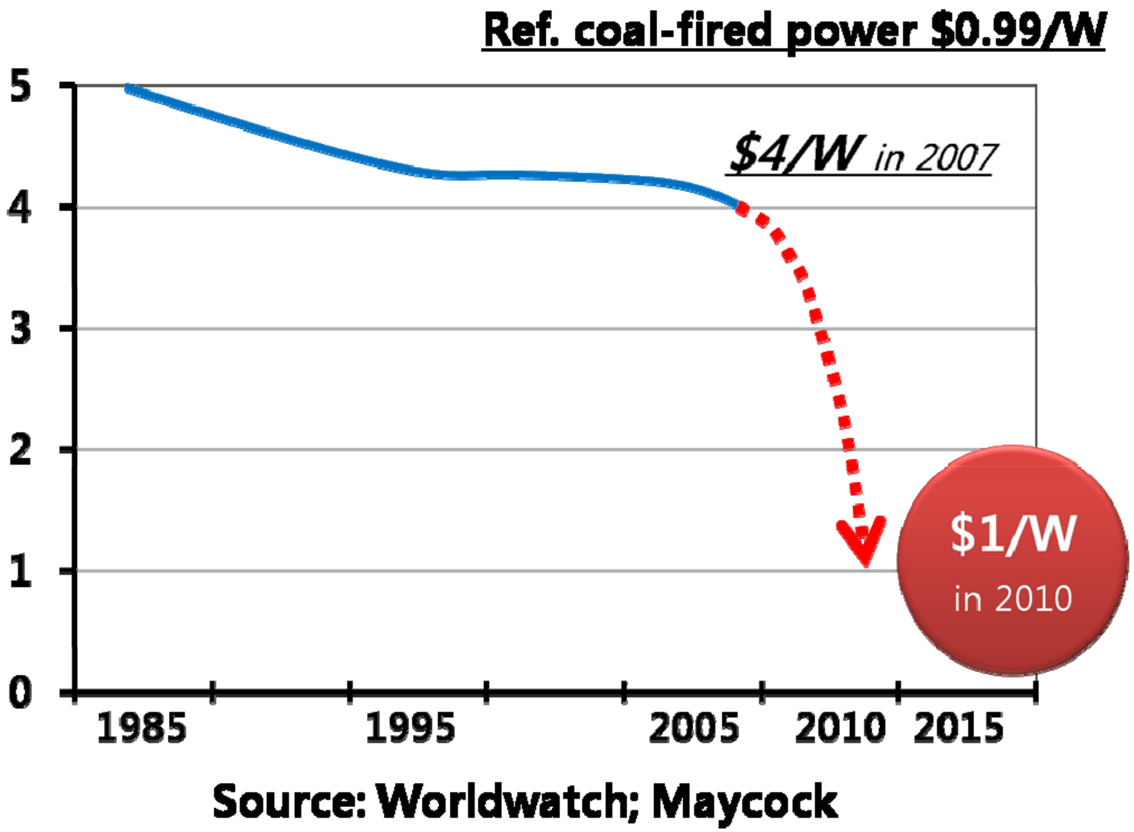
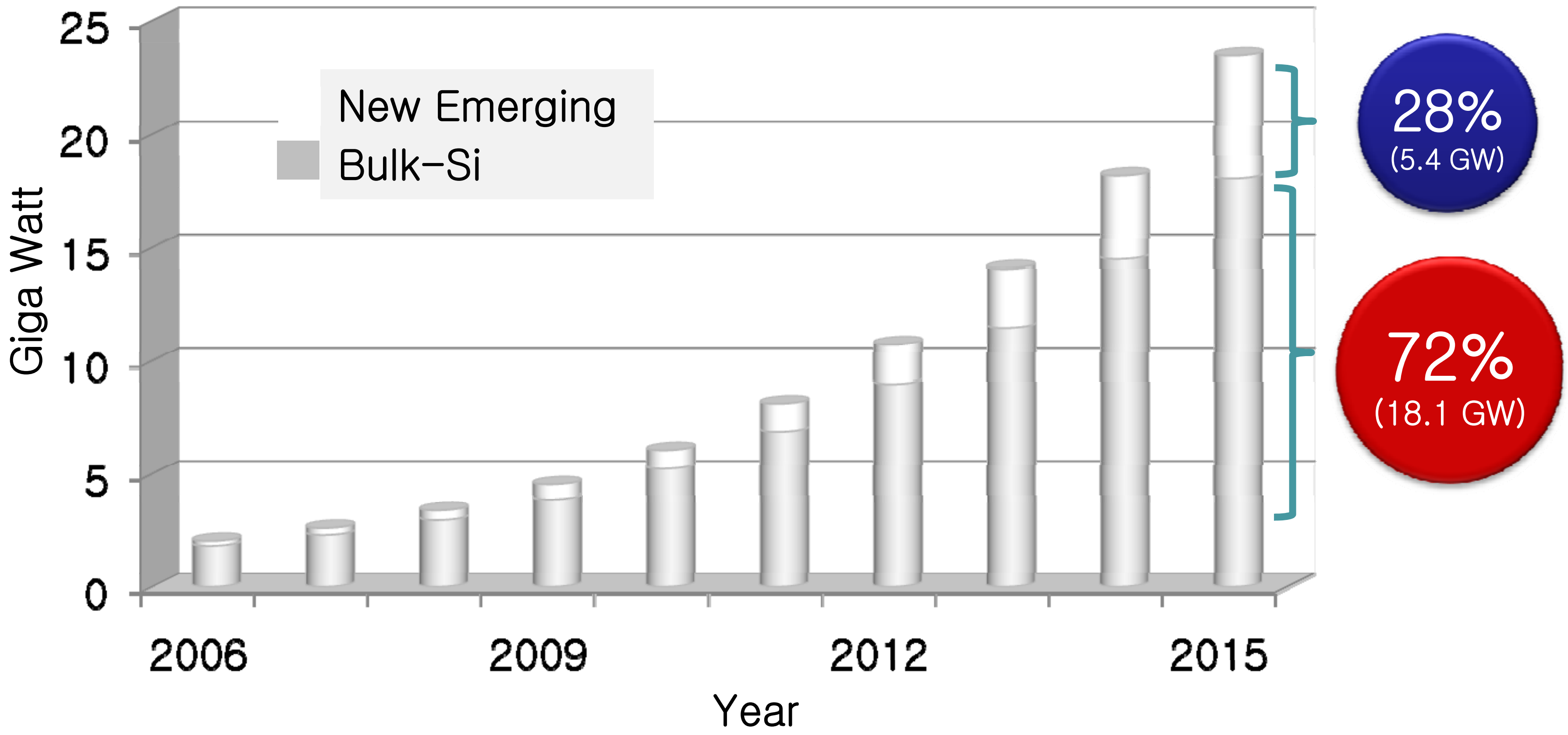


Figure Average cost per watt of PV module 1975-2006.
(Source: Earth Policy Institute, 2007)

Market of Solar Cells

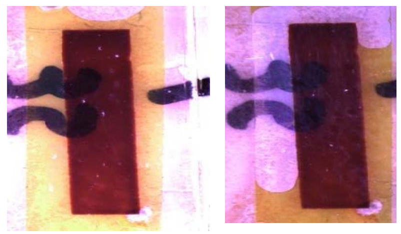


World Market (2011): $ *121.0 billion*
Semiconductor Market (2008): $260.0 billion

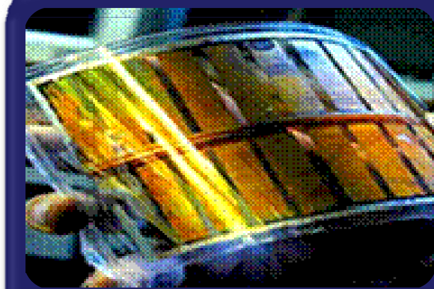
[Solar Annual 2007 (http://www.photon-consulting.com)]
[World Semiconductor Trade Statistics (http://www.wsts.org)]

Why DSSCs?

transparent



durable



flexible

colorful

efficient

Low cost

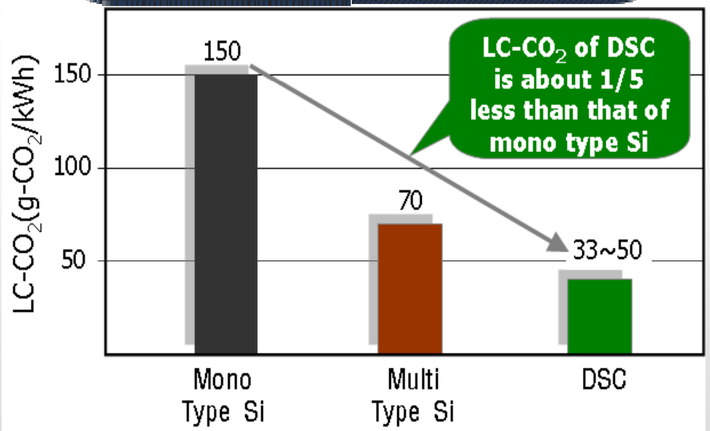
Environmentally Benign

Environmentally friendly

- Low CO_2 emission process
- Non or less toxic materials

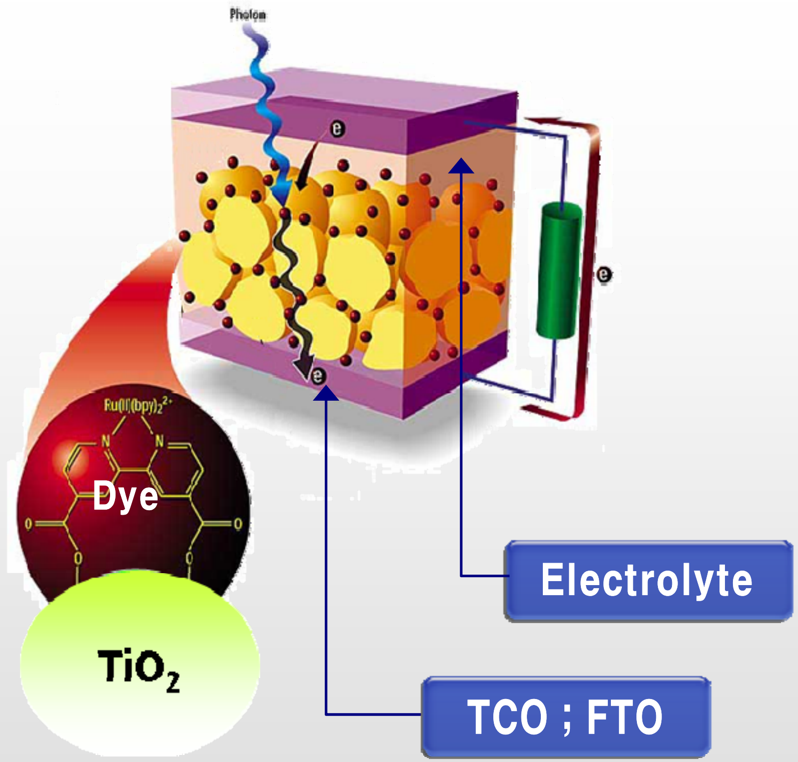
Contribution to CO_2 reduction

Lower CO_2 emission PV



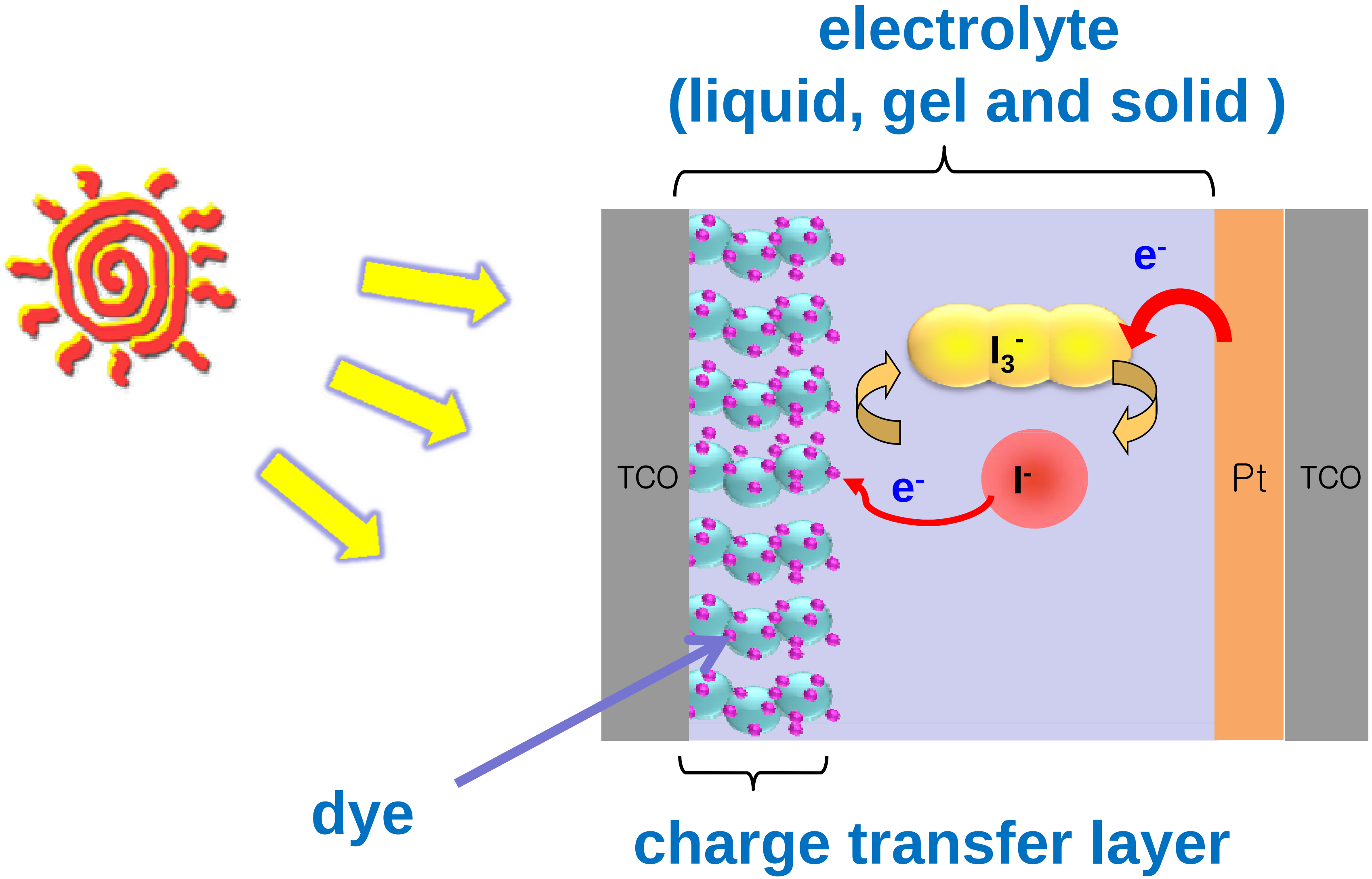
(Toyota Report, PV Expo 2008, Japan)

Eco-frinedly Materials



Non or less toxic materials used

Configuration of DSSC

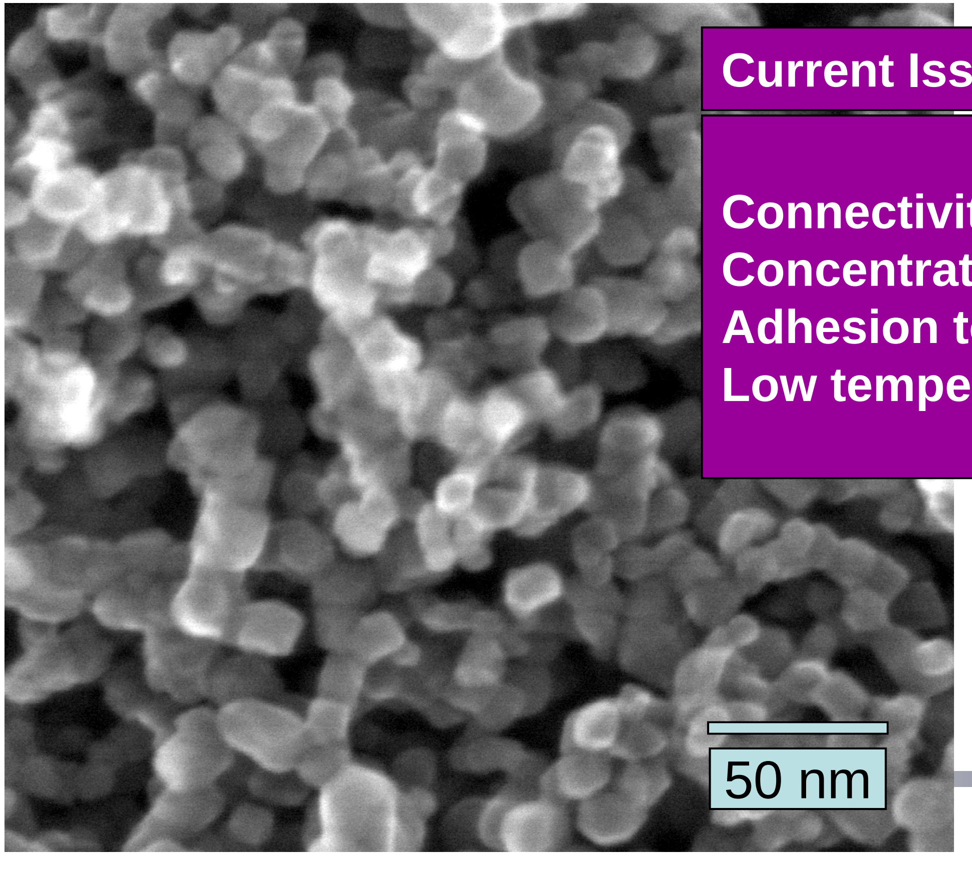


Nanoporous Semiconductor (charge transfer layer): TiO_2 Layer

Issues in semiconductor layer

Basic Requirements:

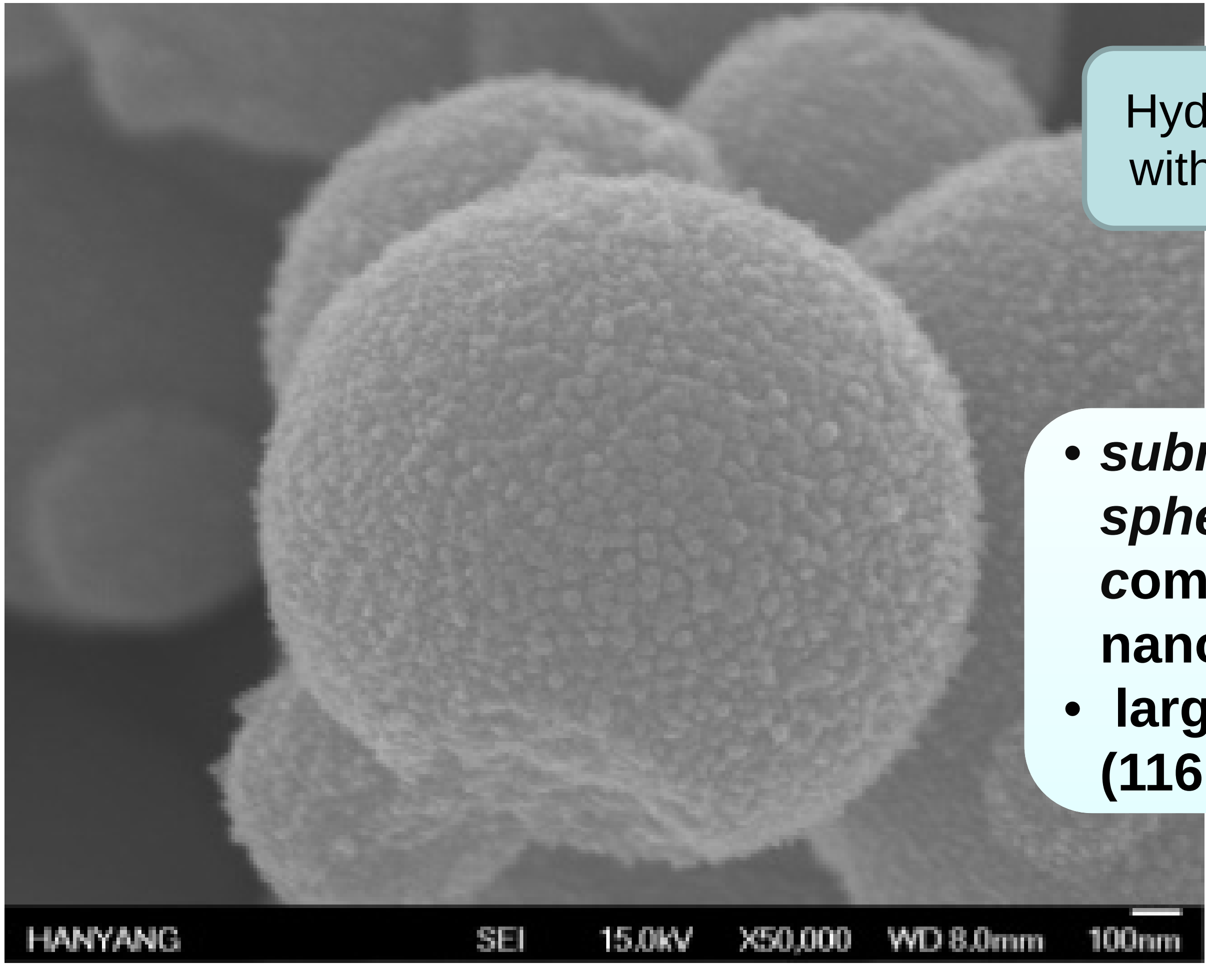
1. **Proper energy level of conduction band**
2. **Wide band gap**
3. **High electron conductivity**
4. **Slow recombination**



Current Issues

Connectivity among nanoparticles
Concentration of surface states
Adhesion to transparent conducting oxide
Low temperature processing

Novel Submicro-Structured TiO_2 Layer

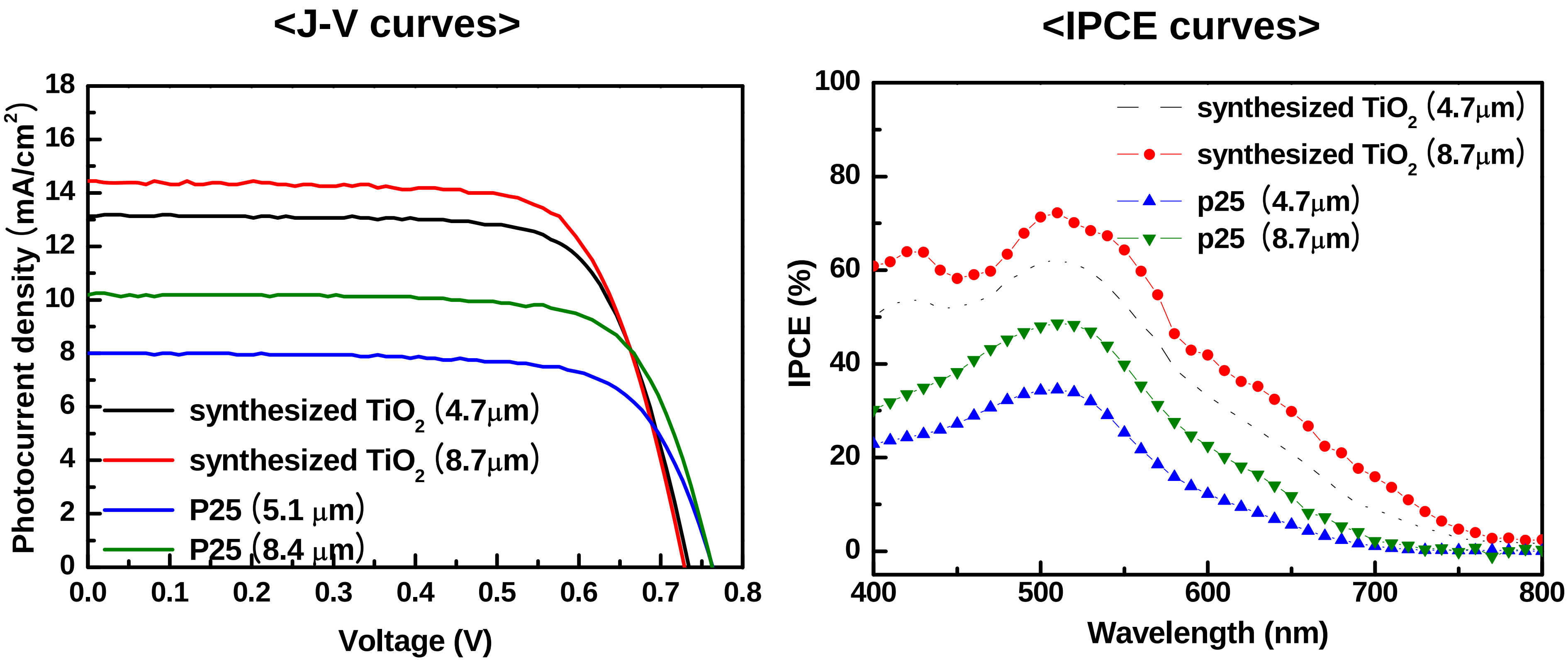


Hydrothermal process : $TiCl_4$ with water, urea and ethanol

- ***submicro-structured spherical TiO_2 particles*** **comprising primary nanoparticles**
- **large surface area (116.49m^2/g) (ref: 77 m^2/g)**

Y. K. Sun et al. *Electrochem. Commun*. (accepted)

Performance of DSSCs



Performance of DSSCs

Sample	P25		Novel TiO_2	
Thickness (μm)	5.1	8.4	4.7	8.7
Adsorbed Dye (× 10^{-7} mol/cm^2)	0.485	0.692	1.05	1.48
Open Circuit Voltage (V_{OC}, mV)	763	763	734	729
Short Circuit Current Density (J_{SC}, mA/cm^2)	7.98	10.21	13.15	14.44
Fill Factor (FF)	72.3	73.1	72.4	71.7
Efficiency (η, %)	4.40	5.69	6.99	7.54

Y. K. Sun et al. *Electrochem. Commun*. (accepted)

Sensitizer : Dye

Issues in dyes

Basic Requirements:

1. **Panchromatic utilizing whole range of visible light (400 ~ 900 nm)**
2. **High IPCE (incident photon-to-current conversion efficiency).**
3. **Strong chemical bonding on semiconductor oxide surface**
4. **Long-term chemical stability**
5. **Low cost**

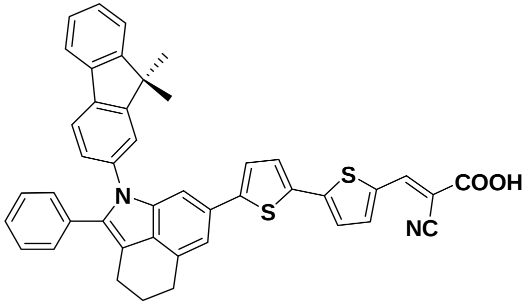
Organometallic Dyes

- **high efficiency:** **(~10.5 % at 100 mW/cm^2)**
- **light absorption mostly from 400-600 nm**
- **rather high cost**

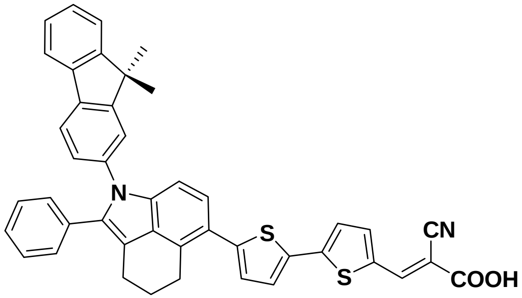
Organic Dyes

- **somewhat low efficiency:** **(7~8 % at 100 mW/cm^2)**
- **low chemical stability**
- **low cost**

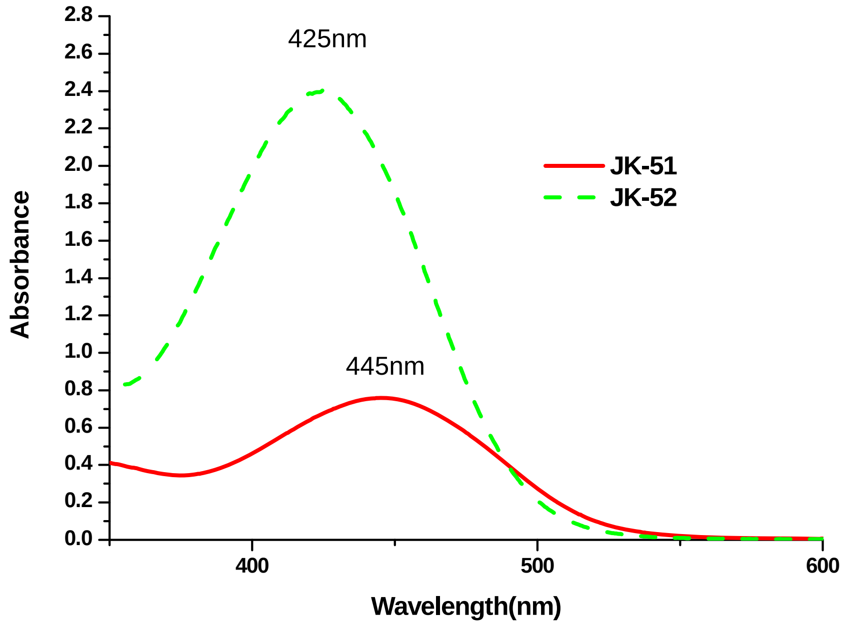
Benzo[cd]indole dyes



JK-51



JK-52



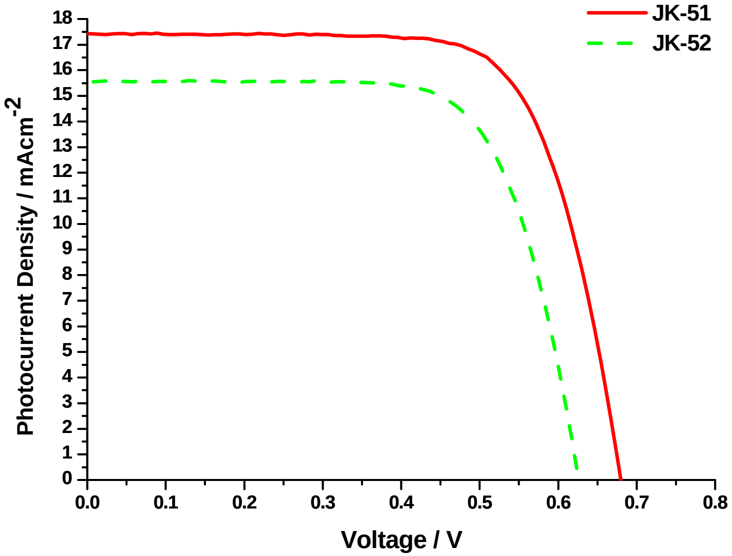
Dye	λ_{abs}/nm (ε/$M^{-1}cm^{-1}$)	E_{ox}/V	E_{0-0}/V	E_{LUMO}/V
JK-51	445 (15188)	1.30 (0.27)	2.38	-1.08
JK-52	425 (48140)	1.53 (0.39)	2.44	-0.91

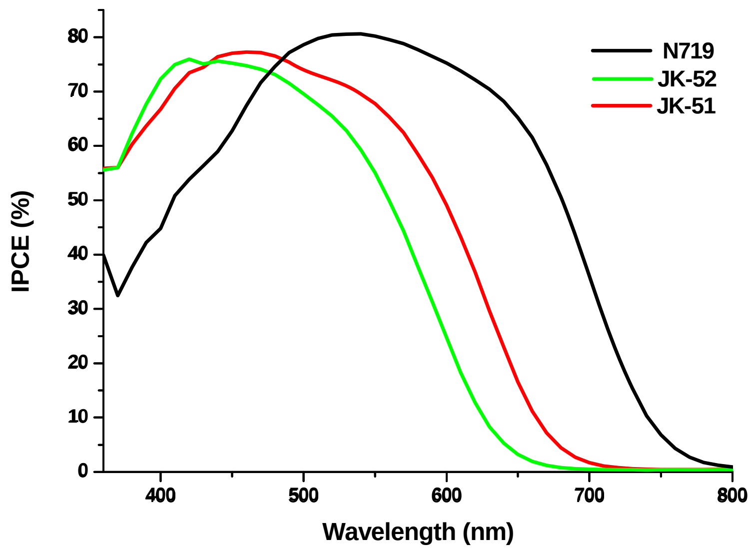
J. Ko et. al. *J. Photochem. Photobiol. A Chem.* 2009, *201*, 102-110

Benzo[cd]indole dyes

J-V curves

IPCE

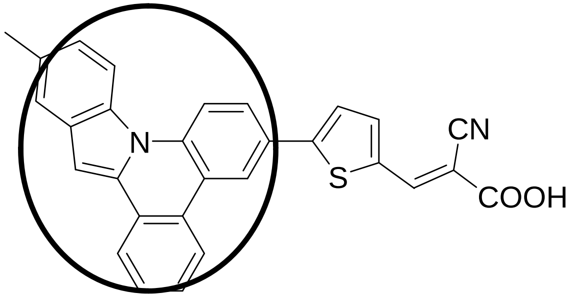




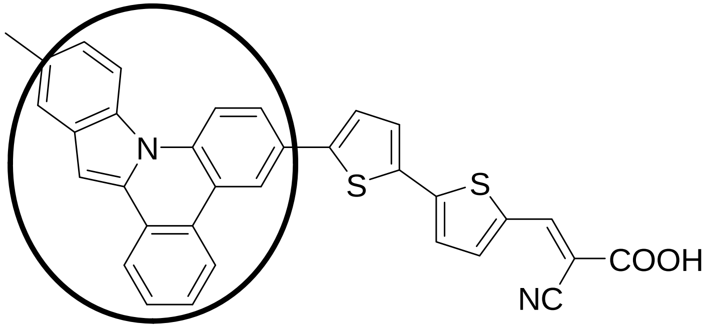
Dye	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η (%)
JK-51	17.43	0.680	0.71	8.42
JK-52	15.56	0.626	0.70	6.88

J. Ko et. al. *J. Photochem. Photobiol. A Chem.* 2009, *201*, 102-110

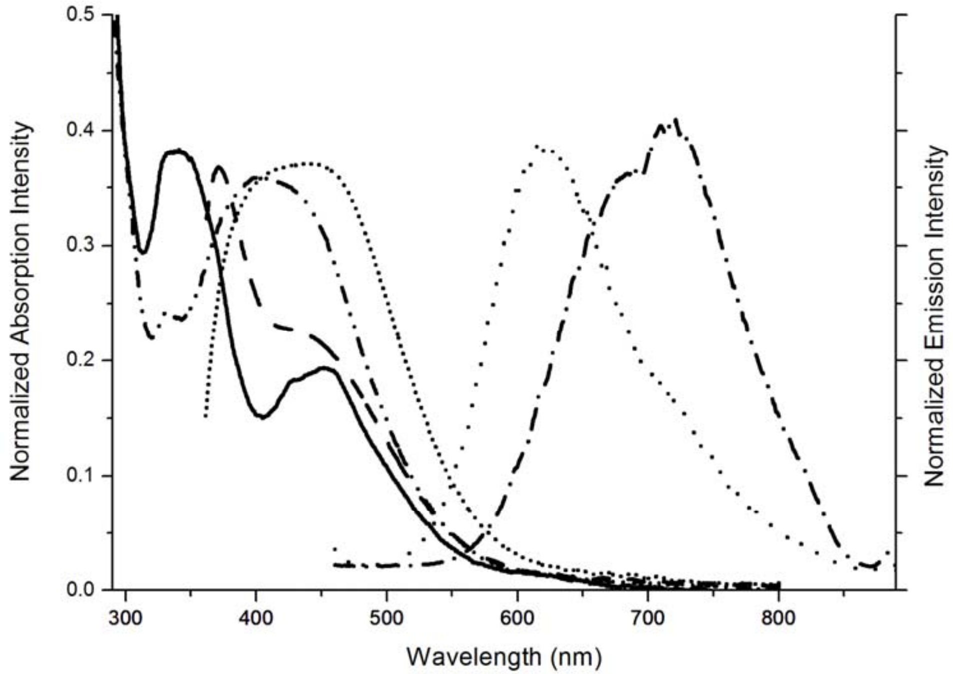
Indolo[1.2-f]phenanthridine dyes



JK-60



JK-61

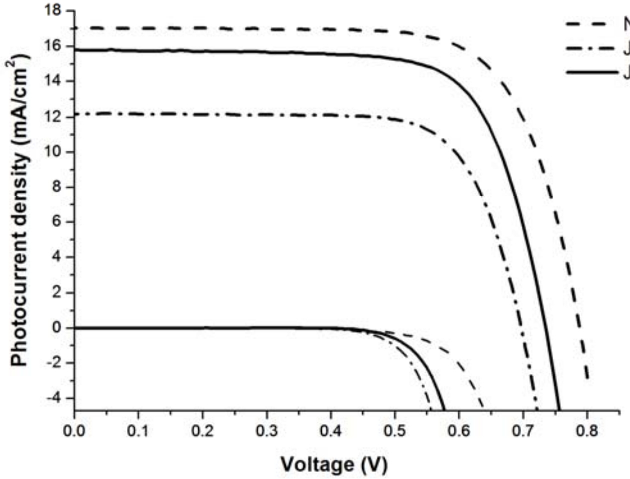


Dye	λ_{abs}/nm (ε/$M^{-1}cm^{-1}$)	E_{ox}/V	E_{0-0}/V	E_{LUMO}/V
JK-60 (soild)	339 (39 400), 453 (22 600)	1.01	2.33	-1.32
JK-61 (dash)	411 (37 600)	1.09	2.19	-1.12

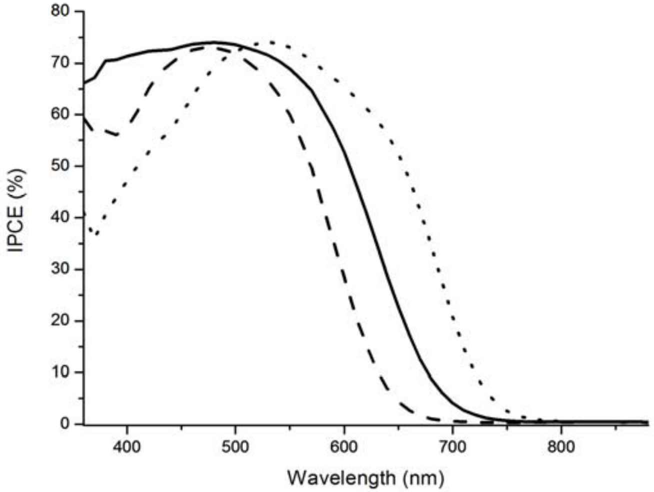
J. Ko et. al. *Tetrahedron* 2009, *65, 5302-5307*

Indolo[1.2-f]phenanthridine dyes

J-V curves



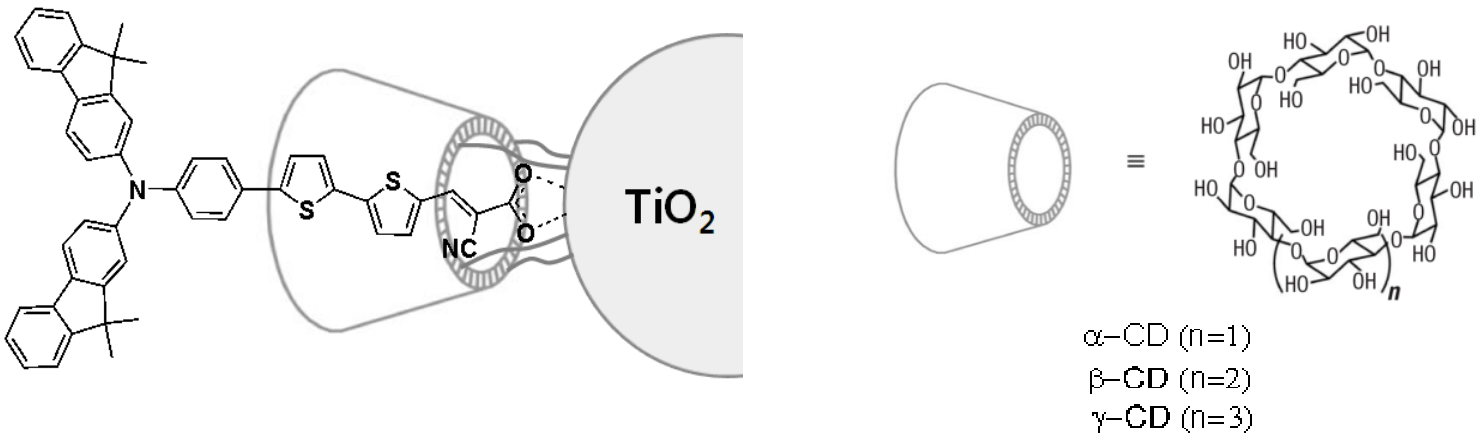
IPCE

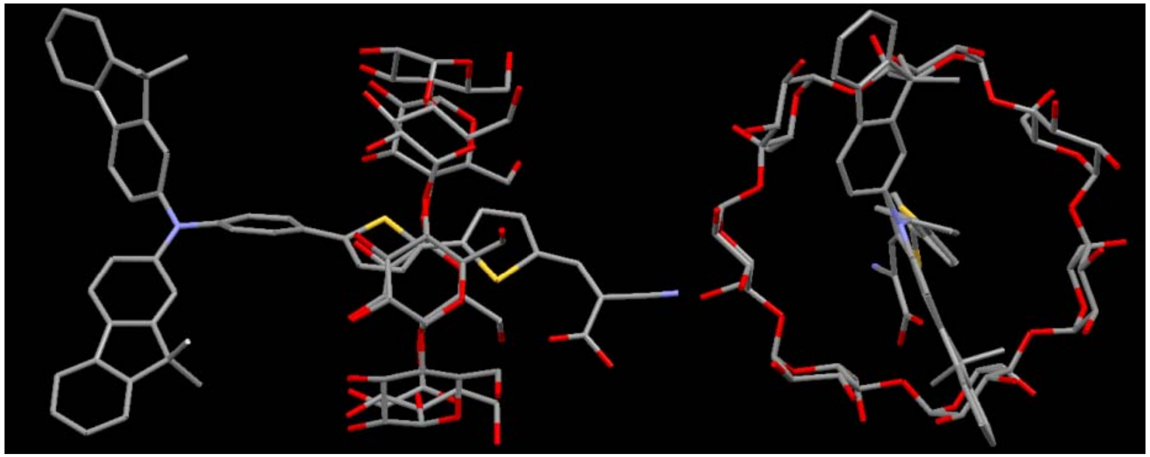


Dye	λ_{abs} [a], nm (ε/dm^{3}mol^{-1}cm^{-1})	E_{ox} [b], V	E_{0-0} [c], V	E_{LUMO} [d], V	J_{sc}, mAcm^{-2}	V_{oc}, V	*FF*	η (%)
JK-60	339 (39 400) 453 (22 600)	1.01	2.33	-1.32	12.17	0.69	0.73	6.22
JK-61	411 (37 600)	1.09	2.19	-1.12	15.81	0.73	0.72	8.34

J. Ko et. al. *Tetrahedron* 2009, *65*, *5302-5307*

Encapsulated dye by Cyclodextrin

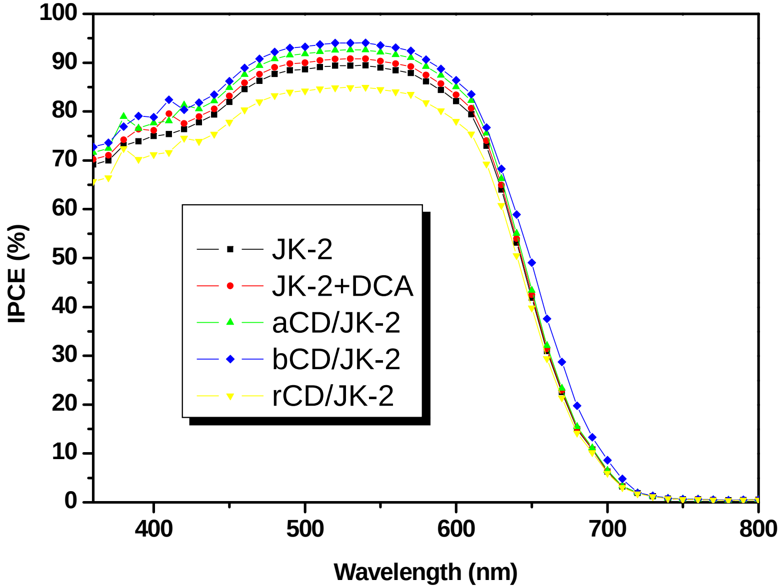




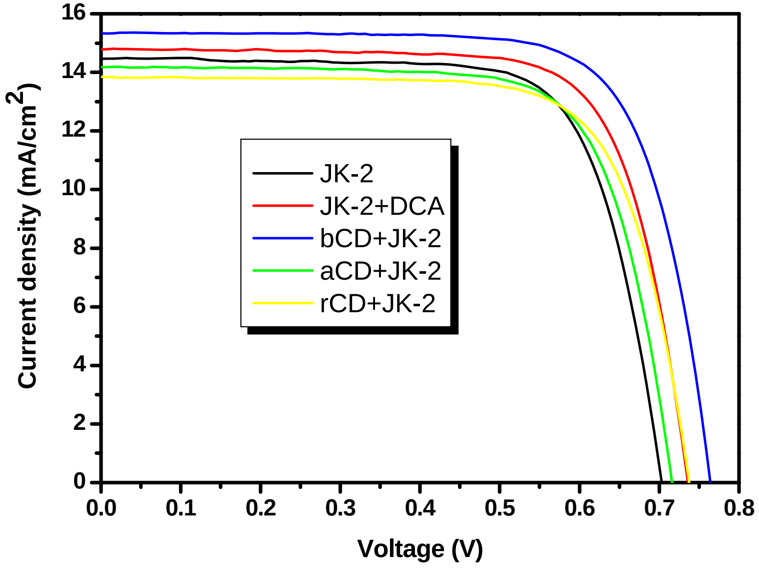
J. Ko et. al. *Angew. Chem. Int. Ed.* 2009*, 48*, 5938-5941

Encapsulated dye by cyclodextrin

IPCE

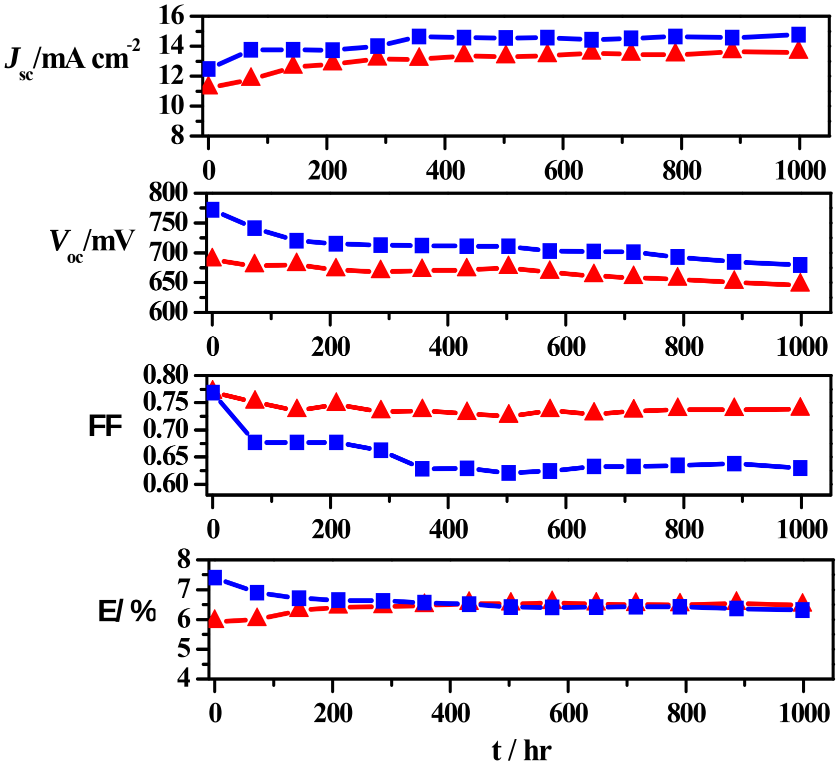


J-V curves



Dye	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η (%)
JK-2	14.51	0.70	0.73	7.42
JK-2+DCA	14.85	0.73	0.74	8.01
α-CD/JK-2	14.26	0.71	0.73	7.41
β-CD/JK-2	15.34	0.76	0.74	8.65
γ-CD/JK-2	13.68	0.74	0.73	7.42

Durability of β-CD/JK-2



Evolution of solar cell parameters with β-CD/JK-2 during visible-light soaking (AM 1.5G, 100 mW/cm^2) at 60 ℃. A 420 nm cut-off filter was put on the cell surface during illumi-nation.

Ionic liquid electrolye (red line): 0.2 M iodine, 0.5 M NMBI, 0.1 M GuNCS in PMII/EMINCS (13/7). Quasi-soild-state electrolyte (blue line): 0.1 M iodine, 0.5M NMBI, 0.6 M DMPII, 5 wt% PVDF-HFP in MPN.

After 1000 h of light soaking

Quasi-soild-state electrolyte

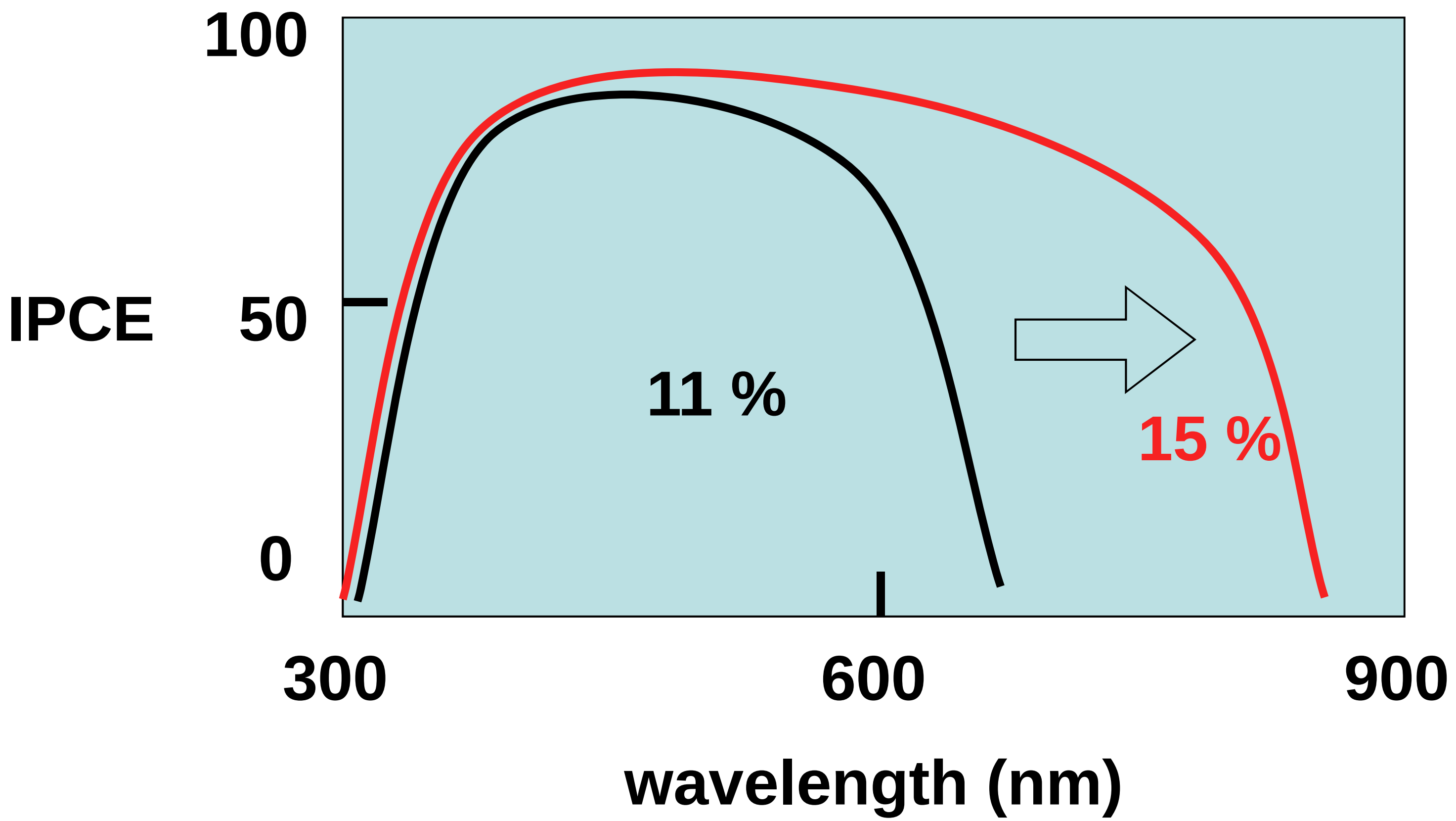
The initial efficiency of 7.40% is slightly decreased to 6.31%

Ionic liquid electrolye

The initial efficiency of 5.93% is slightly increased to 6.48%.

J. Ko et. al. *Angew. Chem. Int. Ed.* 2009, *48*, 5938-5941

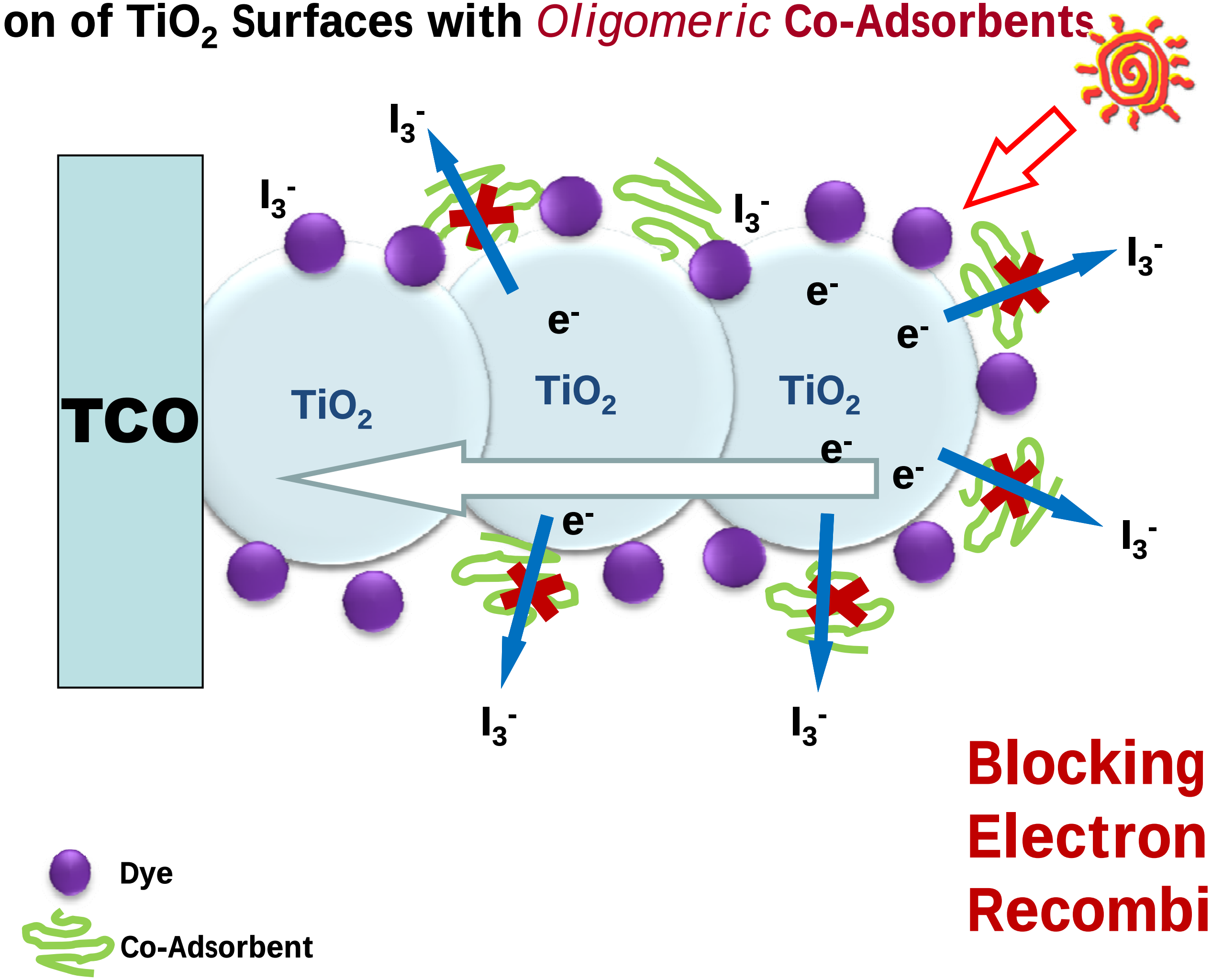
Organic Dyes: Efficiency improvement



Electrolyte Interfaces: blocking electron recombination By coadsorbent

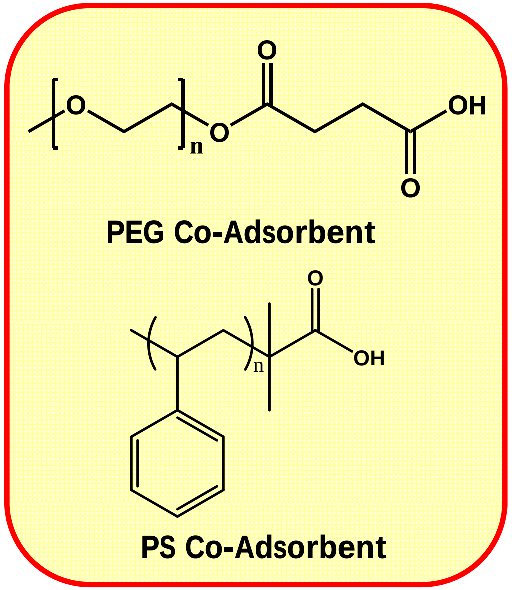
Passivation of TiO_2 Surfaces

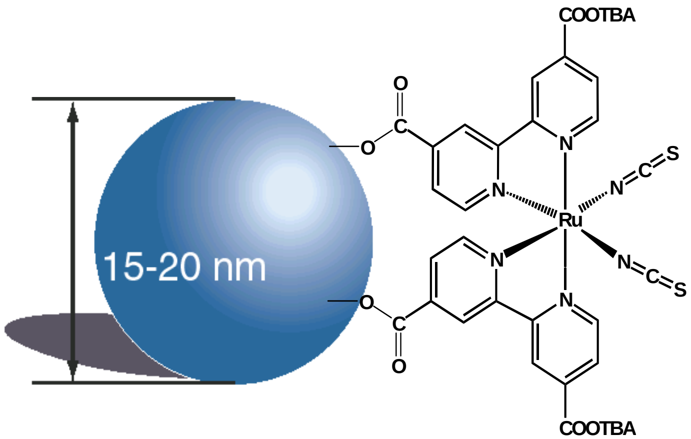
Passivation of TiO_2 Surfaces with *Oligomeric* Co-Adsorbents



Blocking Electron Recombination

Oligomeric Co-adsorbents



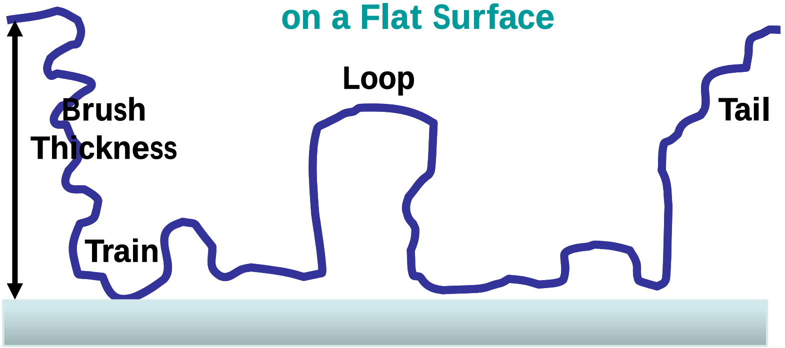


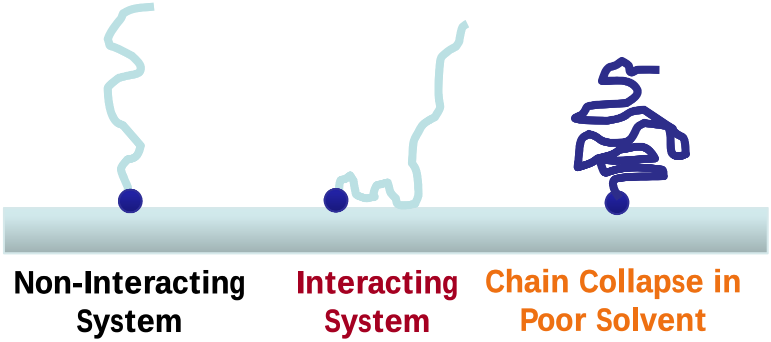
- ✓ Adsorption on vacant TiO_2 sites
- ✓ Blocking electron recombination with I_3^- at TiO_2 electrode / (polymer) electrolyte interfaces
- ✓ Prevention of dye aggregation
- ✓ Band-edge shift
- ✓ Enhancement of TiO_2 pore filling
- ✓ Chain length effect

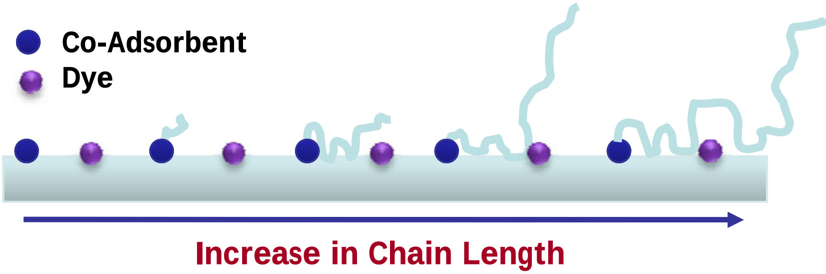
Polymer Adsorption Modes on Flat Surface

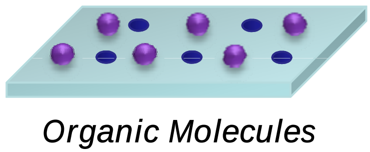
▪ *Polymer Adsorption* **on Flat Surface**

✓ **Chain Conformation of a Single Chain Adsorbed on a Flat Surface**



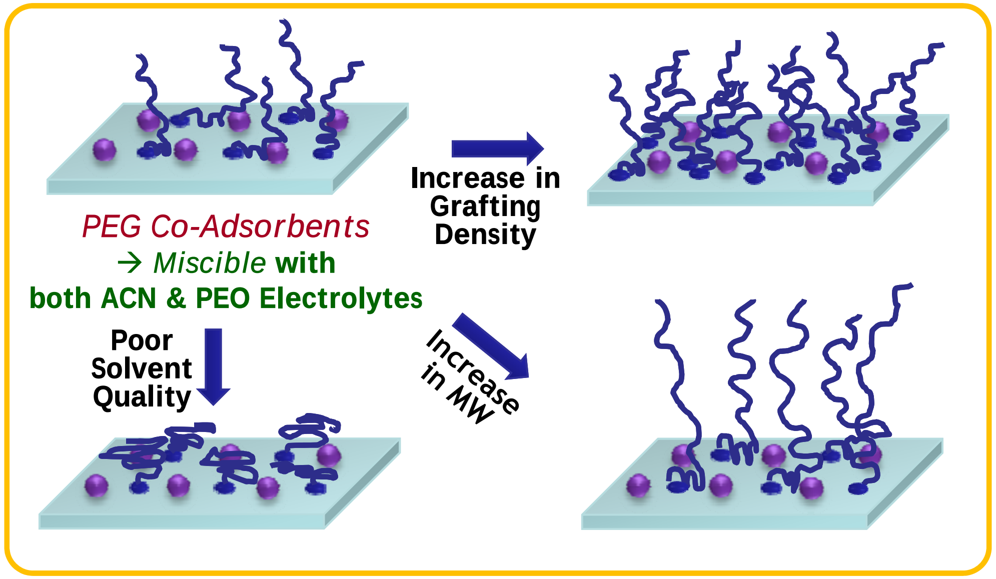


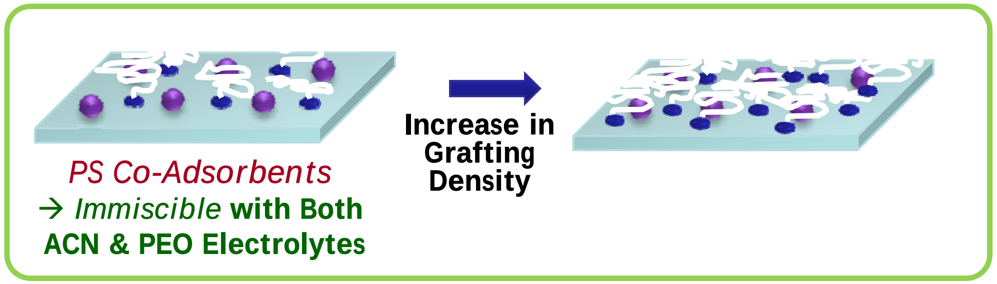




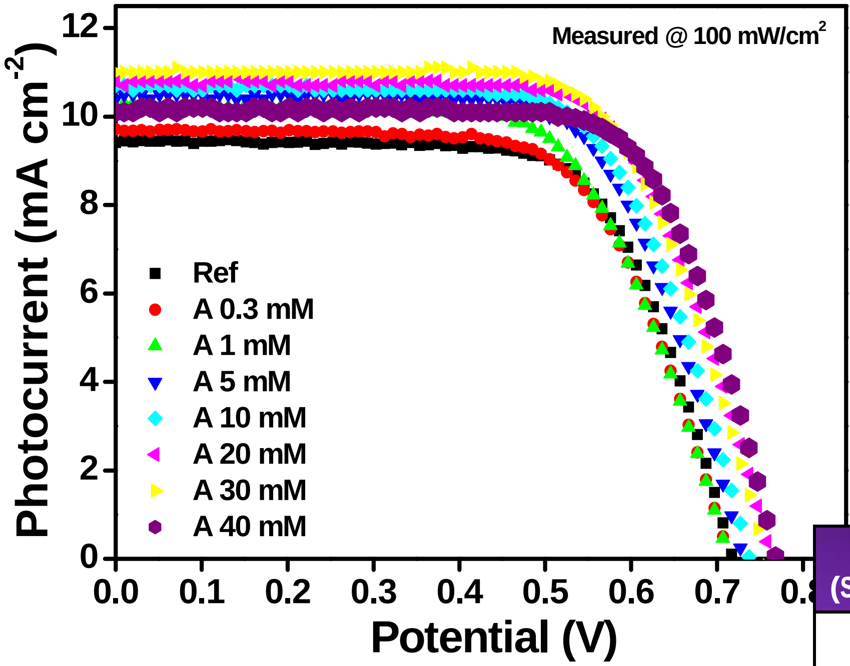
→ *Low Mol Wt Co-Adsorbents* **on TiO_2 surface**

→ **Filling vacant TiO_2 sites & blocking recombination with I_3^- in electrolyte**





Performance of DSSCs with Coadsorbent



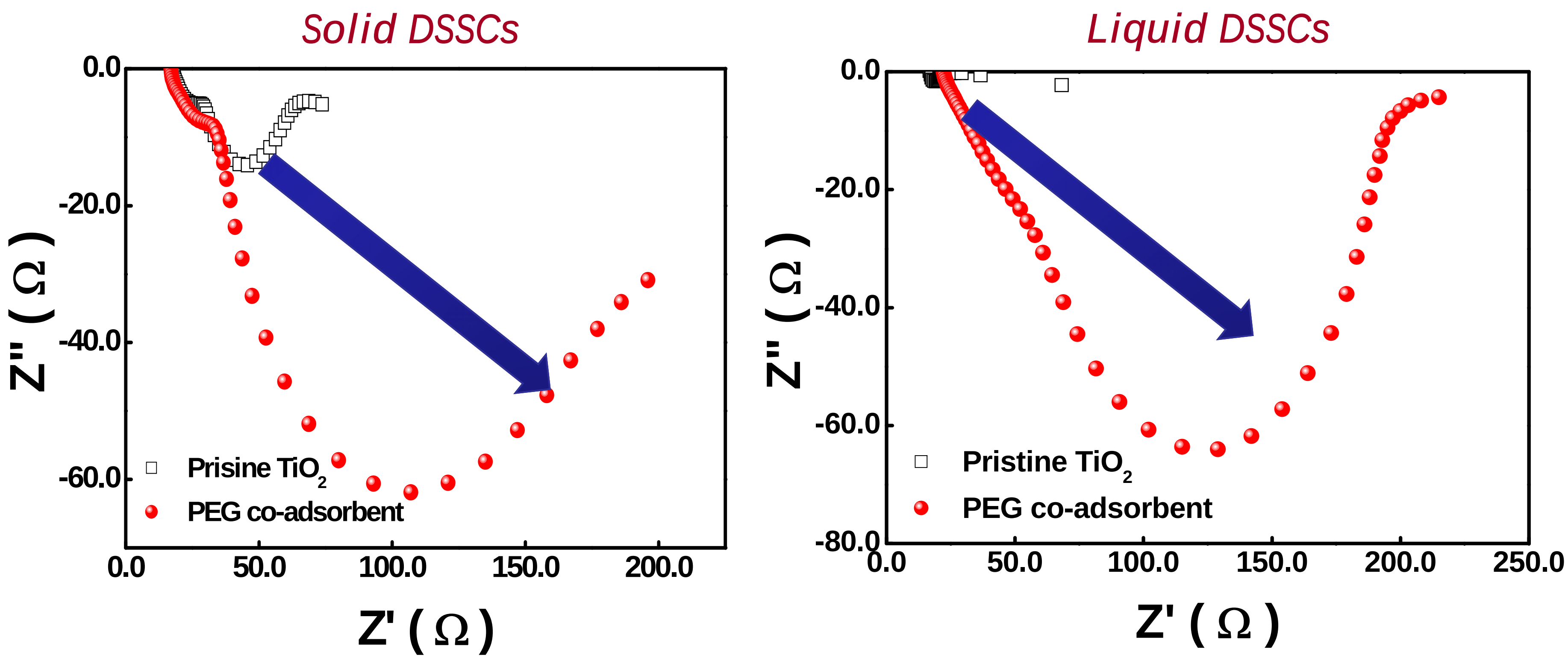
Protocol A (Sequential Adsorption)

A (Sequential)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)
Ref	0.71	9.4	0.68	4.6
0.3 mM	0.71	9.7	0.66	4.6
1 mM	0.71	10.2	0.66	4.8
5 mM	0.73	10.4	0.68	5.2
10 mM	0.74	10.7	0.68	5.4
20 mM	0.76	10.8	0.69	5.6
30 mM	**0.76**	**11.0**	**0.68**	**5.7**
40 mM	0.77	10.1	0.71	5.6

- Dye : 0.3 mM N719 in ACN/tert-BuOH (1:1 v/v)
- Co-adsorbent : 0 ~ 40 mM in ACN/tert-BuOH (1:1 v/v)
- Electrolyte : 0.5 M MPII + 0.05 M I_2 in MPN
- TiO_2 film thickness : 12 μm, Active area : 0.25 cm^2
- Measured under AM 1.5, 100 $mWcm^{-2}$ with shading mask

Suppressed Electron Recombination

- Electrochemical Impedance Spectroscopy (EIS)



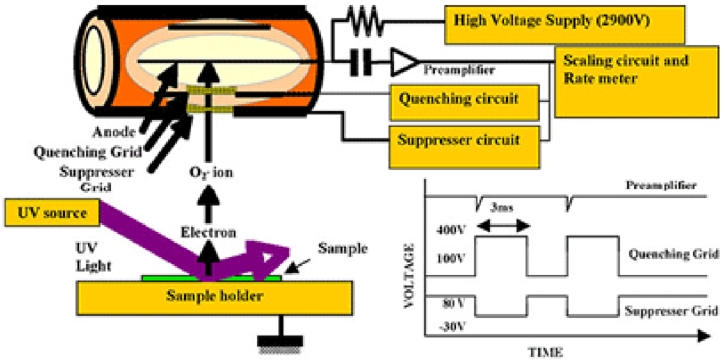
under *Dark* Condition

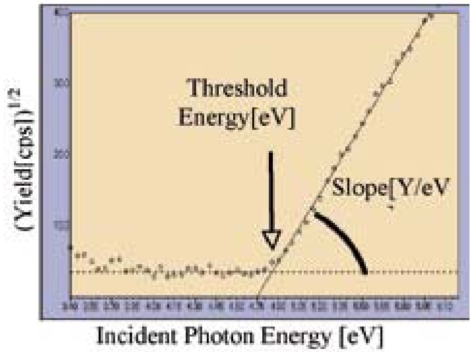
✓ *Suppressed Electron Recombination* **at TiO_2 Electrode / Electrolyte Interfaces**

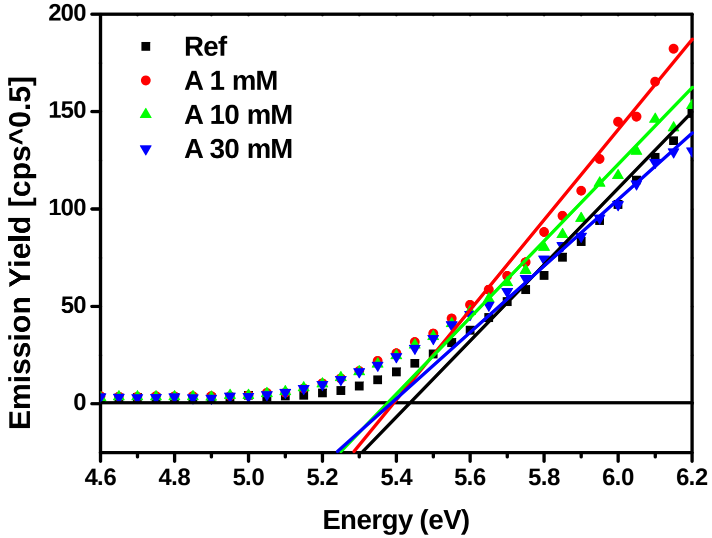
Upward Shift of Band Edge

- Measurement of Band-Edge Shift of TiO_2 Electrodes

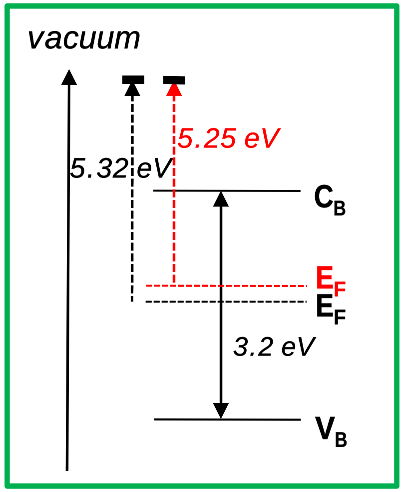
Photoelectron Spectrometer (AC-2)







Concentration of co-adsorbent	Work function (eV)
Reference	5.32 eV
A 1 mM	5.29 eV
A 10 mM	5.26 eV
A 30 mM	5.25 eV



→ *Band-edge shift* less negatively

Summary

1. Novel Submicro-Structured TiO_2 Layer with High Surface Area.

2. New Highly Efficient and Durable Organic Dyes.

3. Coadsorbents to Block Electron Recombination and to Shift the Band Edge Upward.

Acknowledgements

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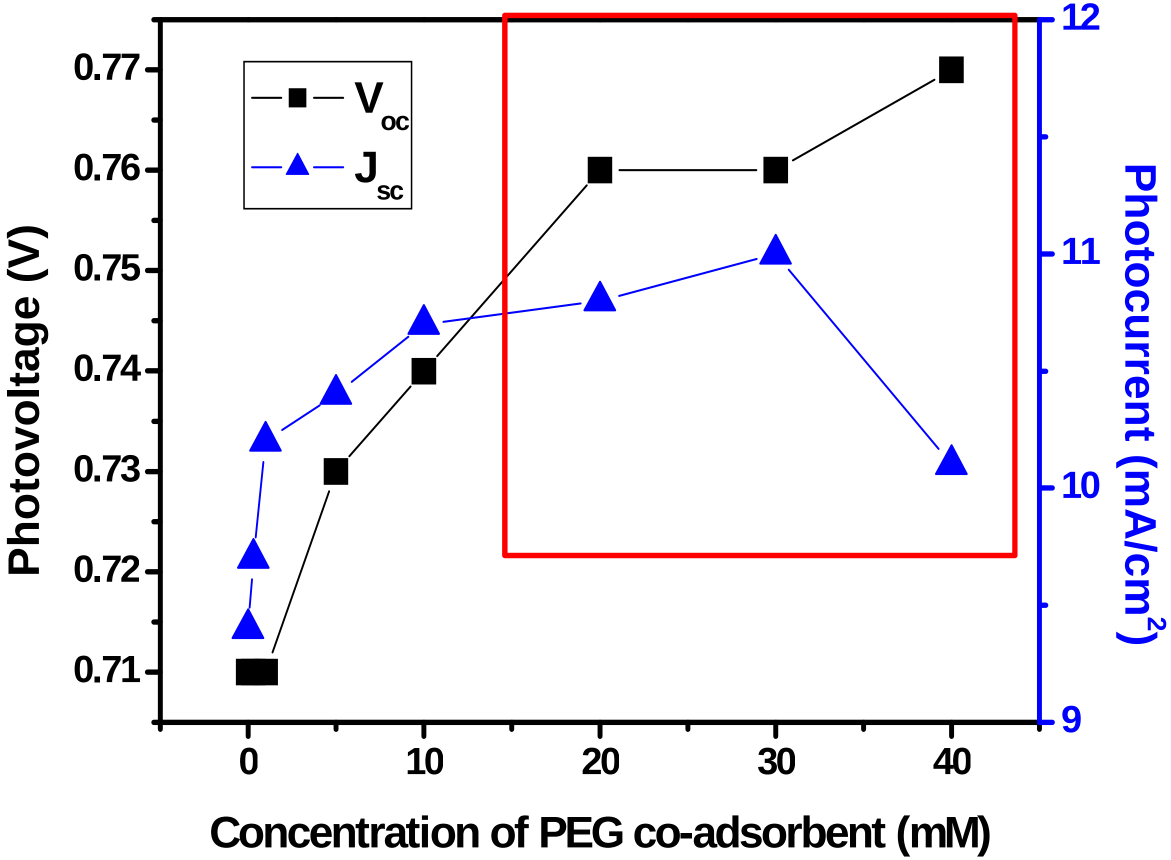
Prof. Yang Kook Sun (Hanyang U.)
Prof. Kookheon Char (Seoul National U.)

Students:
Seoul National U. (Yong Gun Lee)
Hanyang U. (June Hyuck Jung, Suil Park, Donghoon Song, Tae Wook Son)

Thank you very much

Performance of DSSCs

- *Protocol A (Sequential Adsorption)*



J-V Data of DSSCs as a Function of Concentration of PEG-Based Co-Adsorbent