Dye-sensitized solar cells

(DSSCs)

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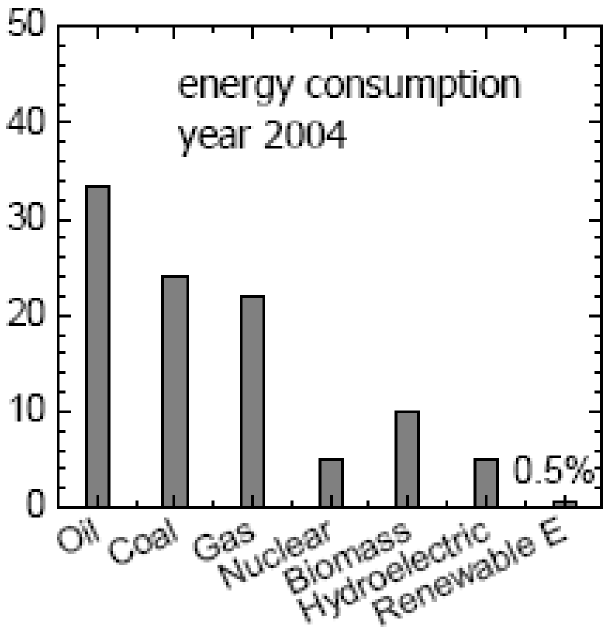
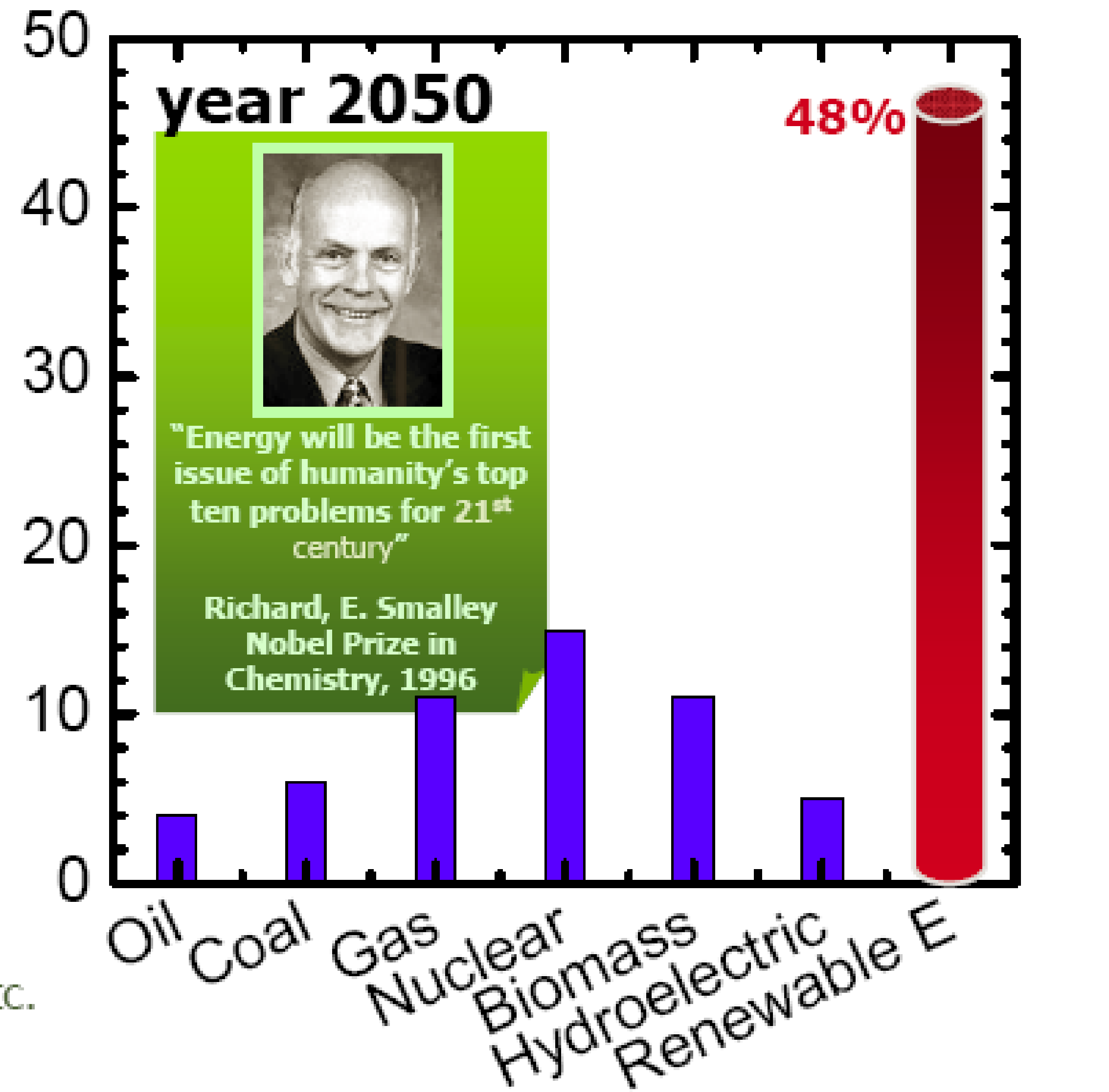
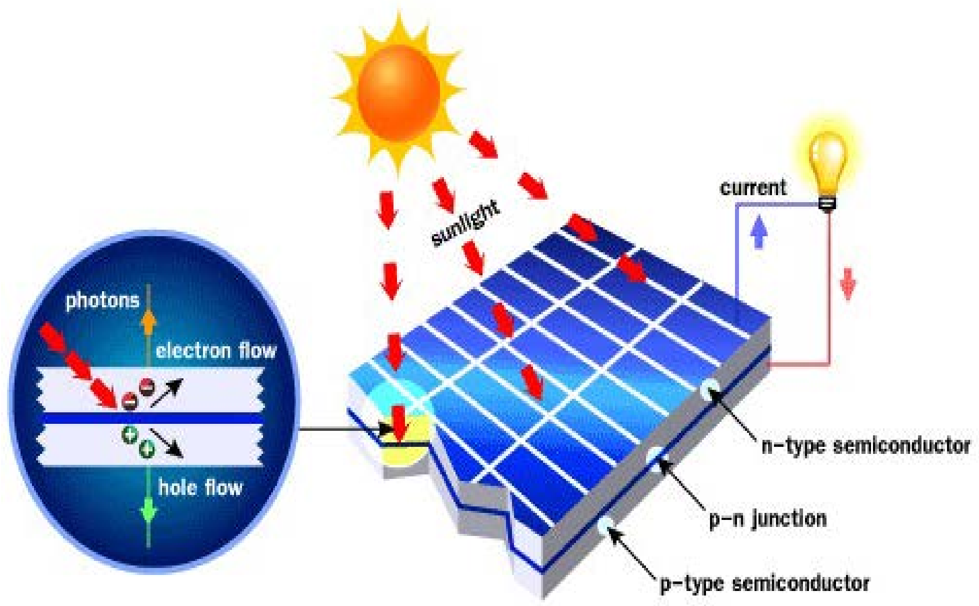
Paradigm for Energy





*Renewable Energy
= Solar Wind, Geothermal etc.

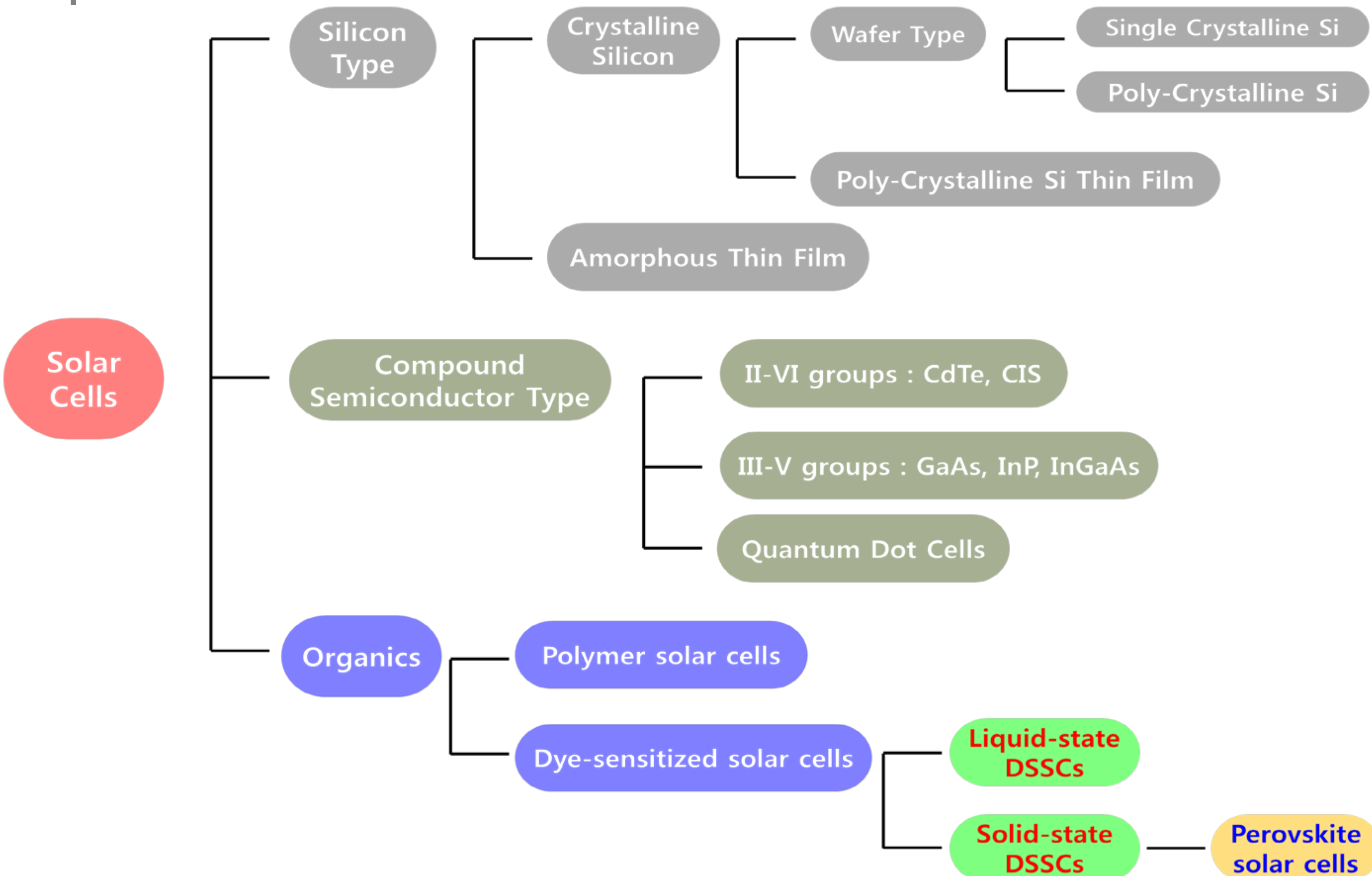
What is Solar Cells?



When sunlight is absorbed by some materials, the solar energy knocks electrons loose from their atoms, allowing the electrons to flow through the material to produce electricity. This process and device of converting light (photon) to electricity (voltage) is called the photovoltaic (PV) effect and solar cell, respectively.

Light Energy (photons) → Electrical Energy

Types of Solar Cells



Why DSSCs?

Transparent
& Colorful

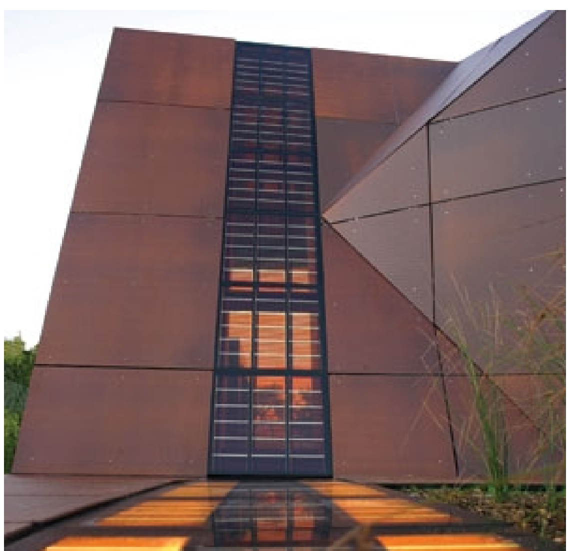
Flexible

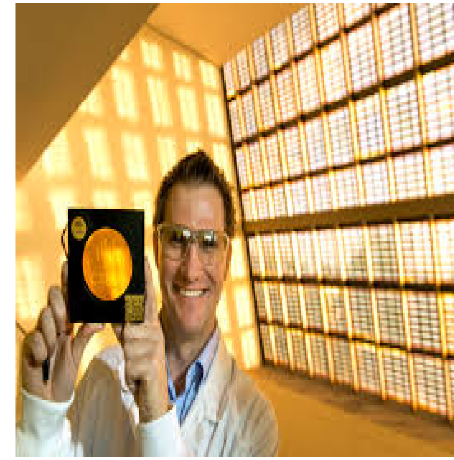
Low Cost

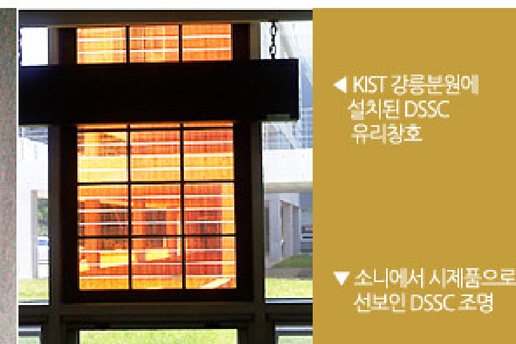
Large Area

From KIST Dye-sensitized Solar Cell Technologies
Dyesol Dye-Sensitized Solar Panel Incorporated into Tata Steel Roof Panel

Potential Market of DSSCs

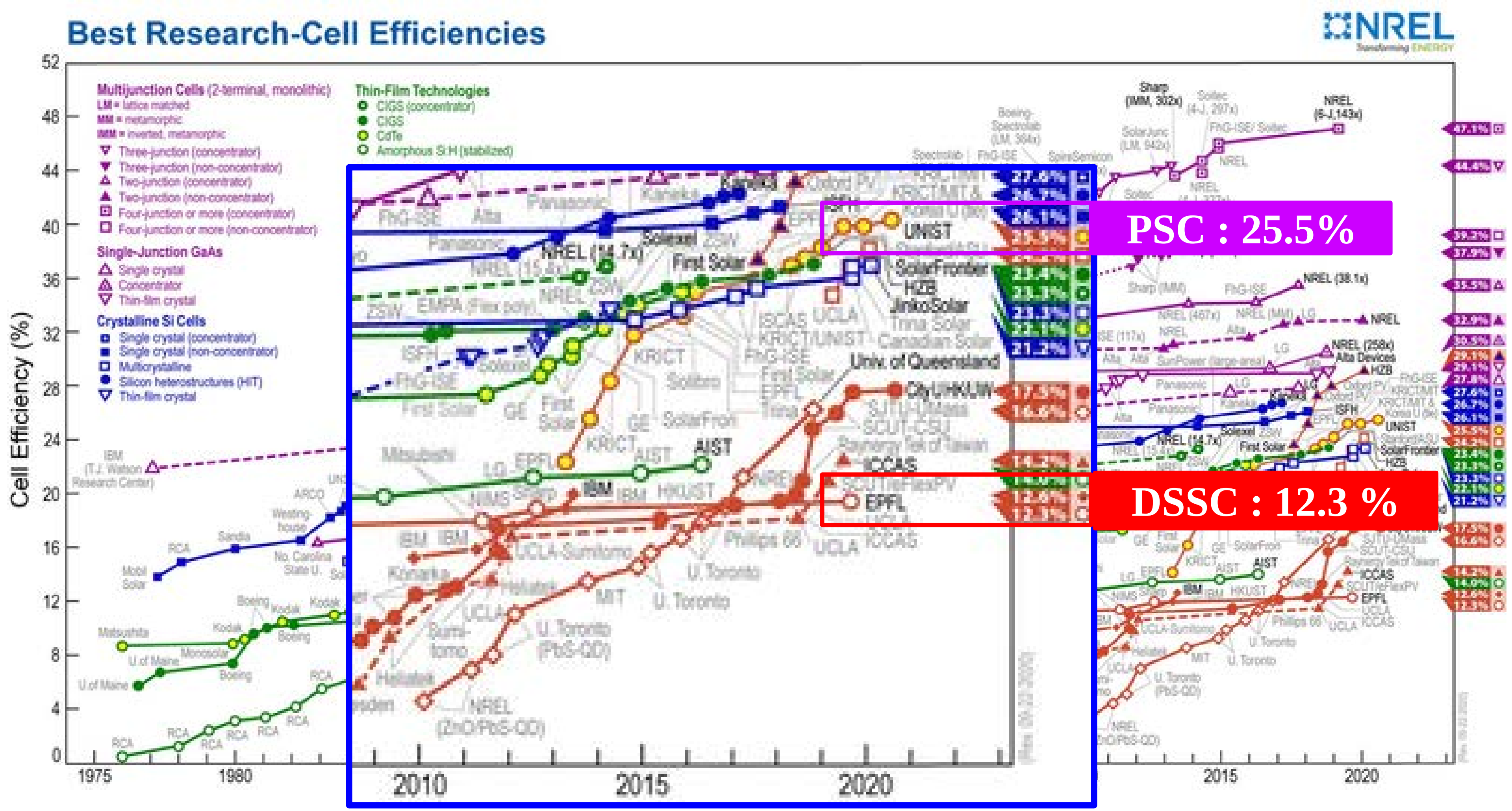




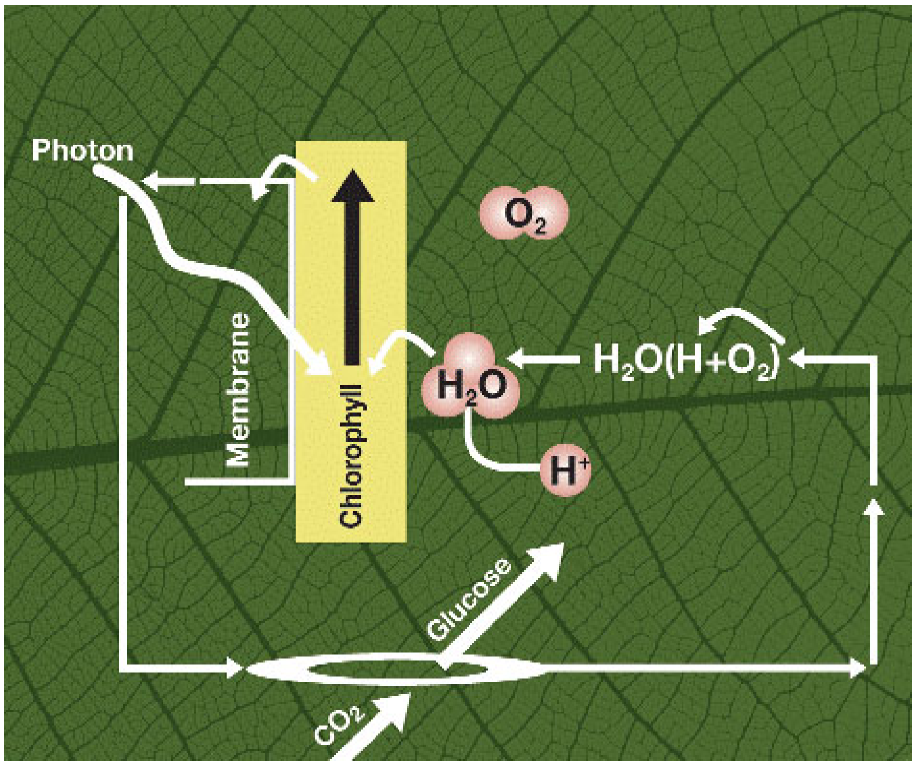


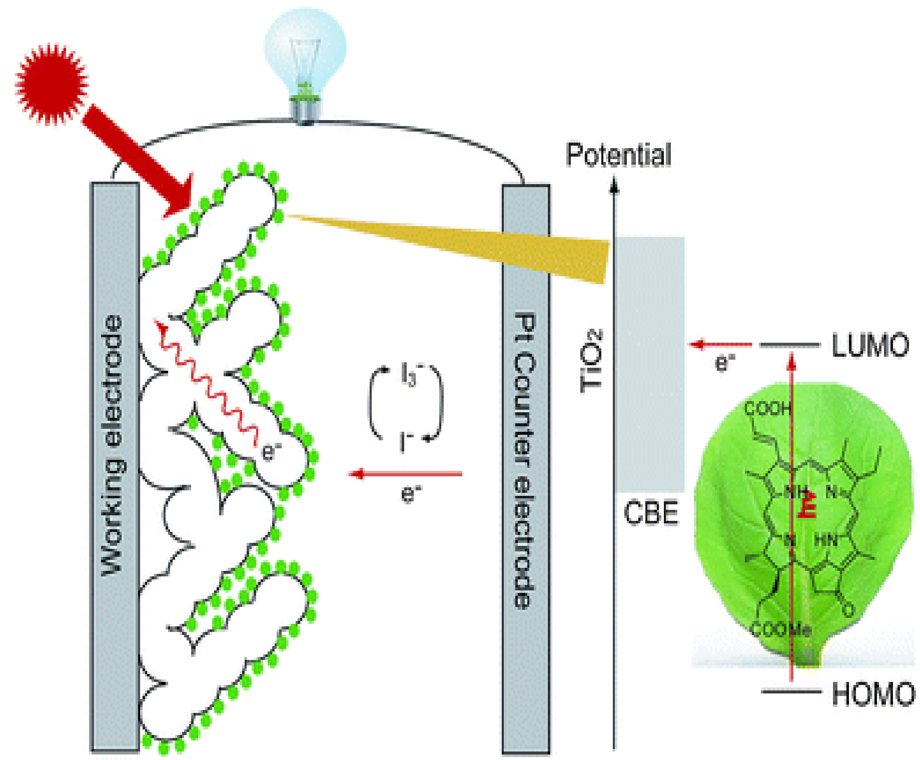
From DyeSol and Samsung

Best Research-Cell Efficiencies



Photosynthesis vs DSSCs

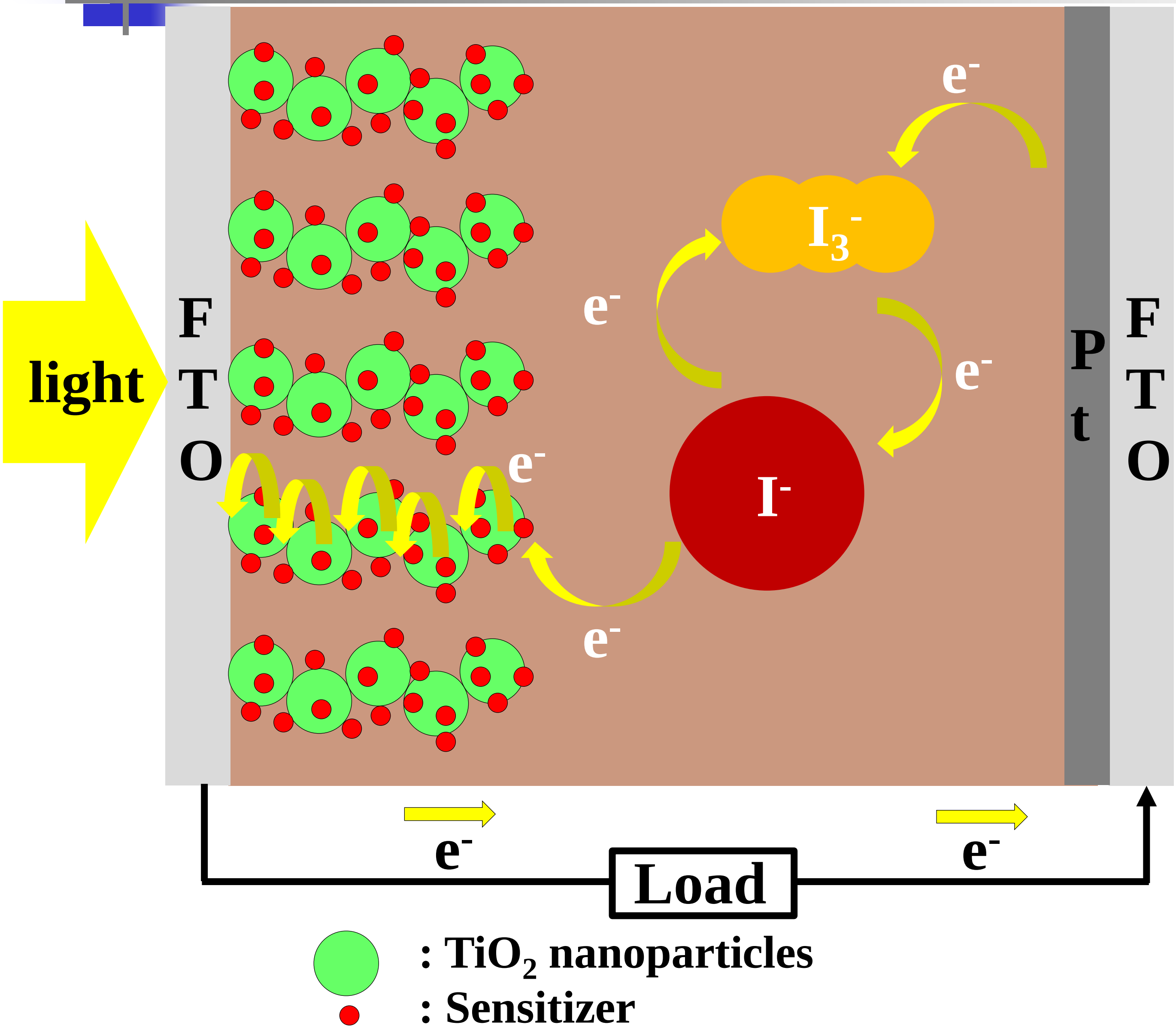




www.dyesol.com

Schematic presentation of the working mechanism of a dye-sensitized solar cell based on chlorophyll

Principle of DSSCs



1. Photon + Dye

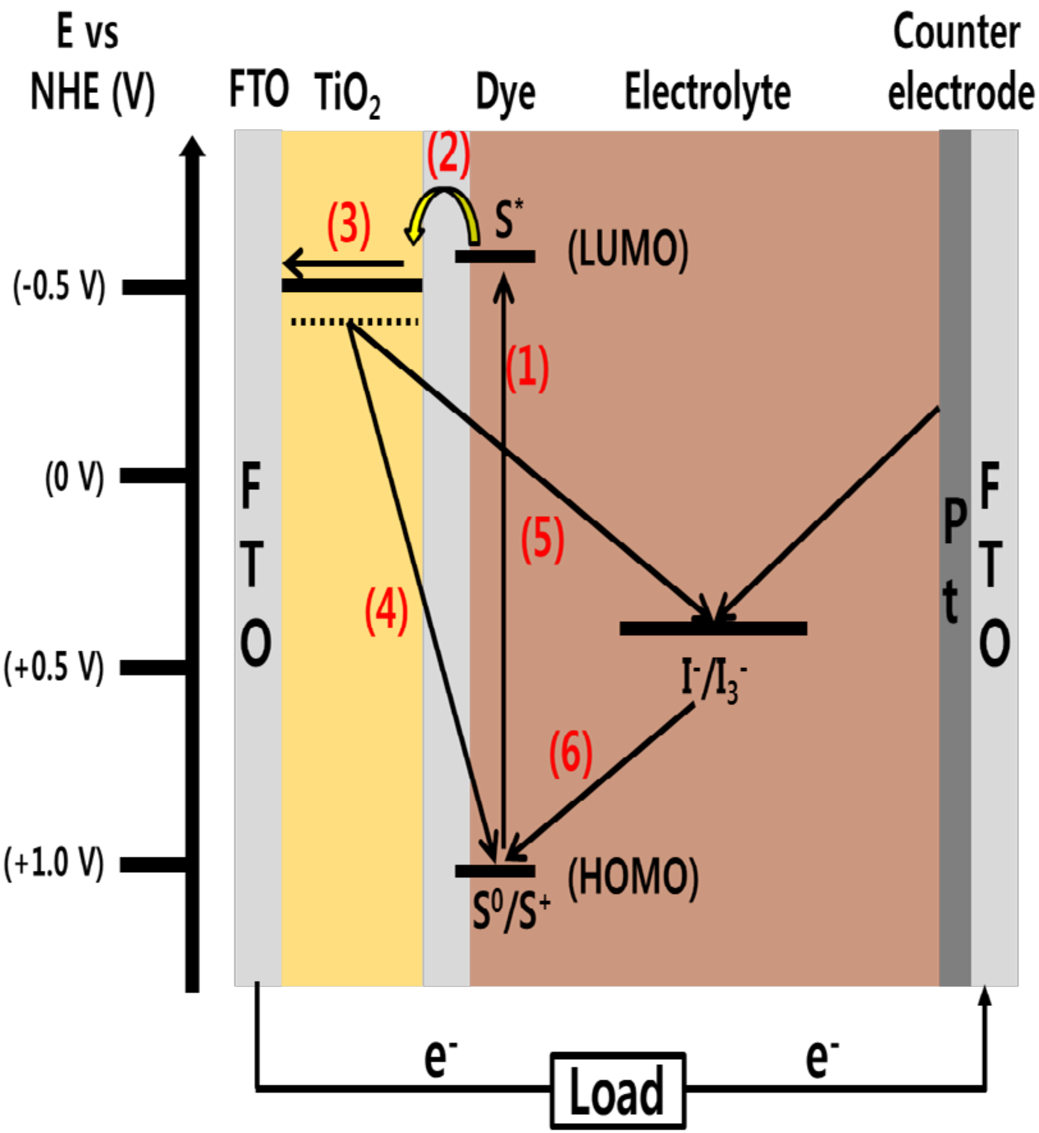
   → $Dye^+ + e^-$
2. Electron transport to TiO_2 nanoparticles
3. Electron circulation
4. Reduction :

   $2e^- + I_3^- \rightarrow 3I^-$
5. Oxidation :

   $2Dye^+ + 3I^-$

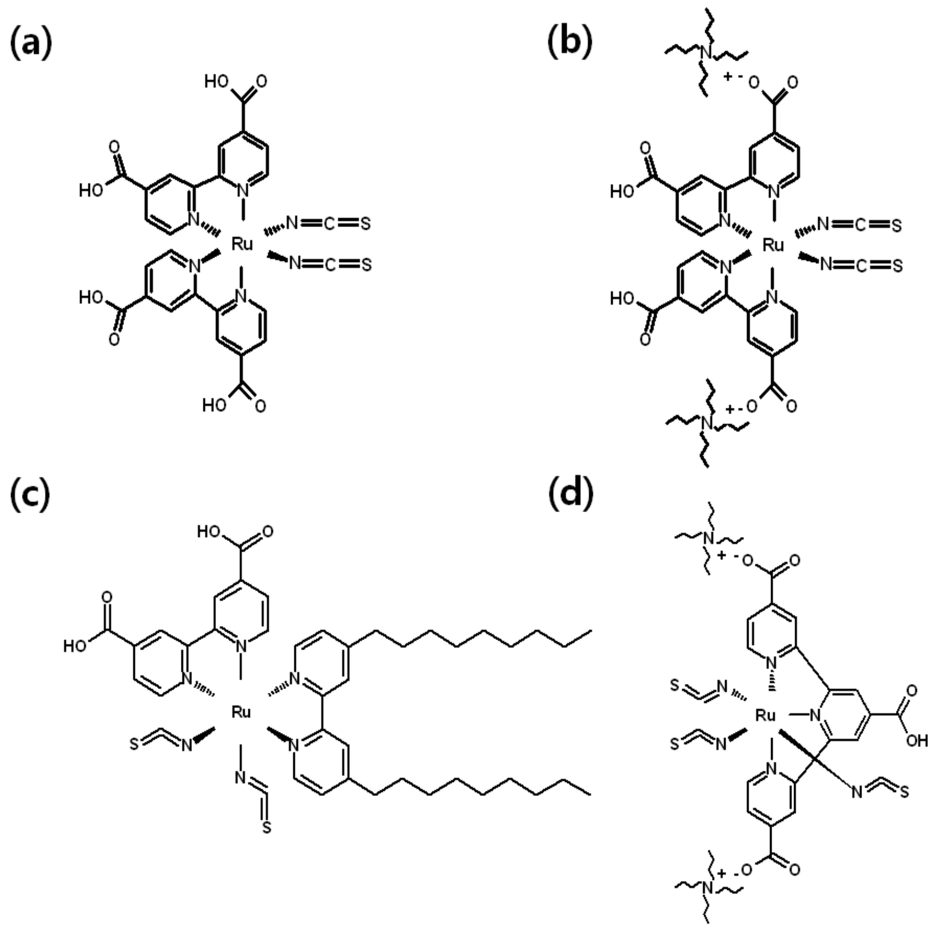
   $\rightarrow I_3^- + 2Dye$

Electron Transfer Rates of DSSCs



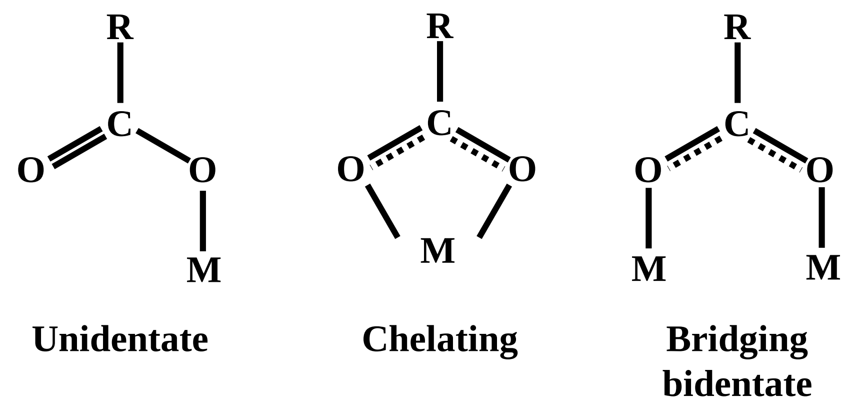
1. Excitation of the dye (ns)
2. Electron injection from dye into conduction band of nanoporous TiO_2 (ps)
3. Electron diffusion through nanoporous TiO_2 (ms)
4. Recombination of injected electron with oxidized dye (s)
5. Recombination of injected electron with oxidized redox couple (ms)
6. Regeneration of the dye by electron transfer from redox couple (10 ns)

Ru Dyes and Bonding on TiO_2 Surface



(a) N3, (b) N719, (c) Z907, and (d) Black dye

Chemical Bondings between TiO_2 and Dyes

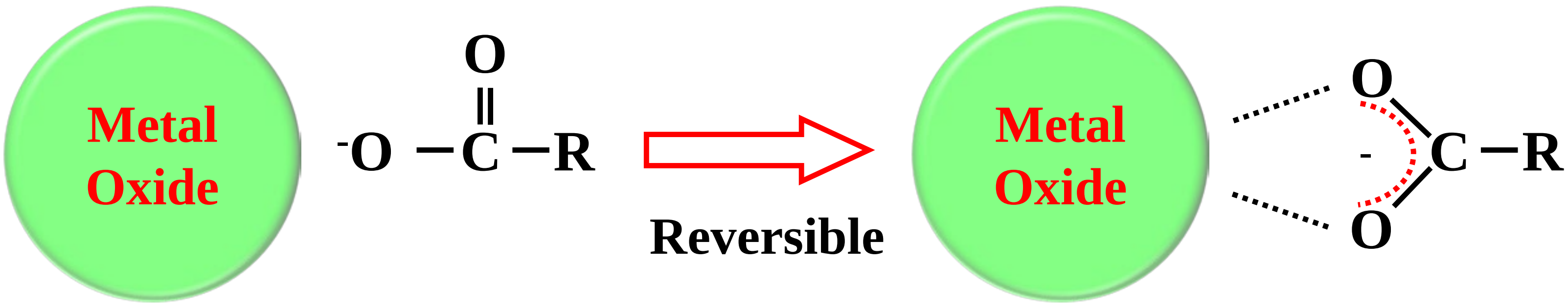


Molar Extinction coefficient of dyes

N719 : 14.0×10^3 $M^{-1}cm^{-1}$

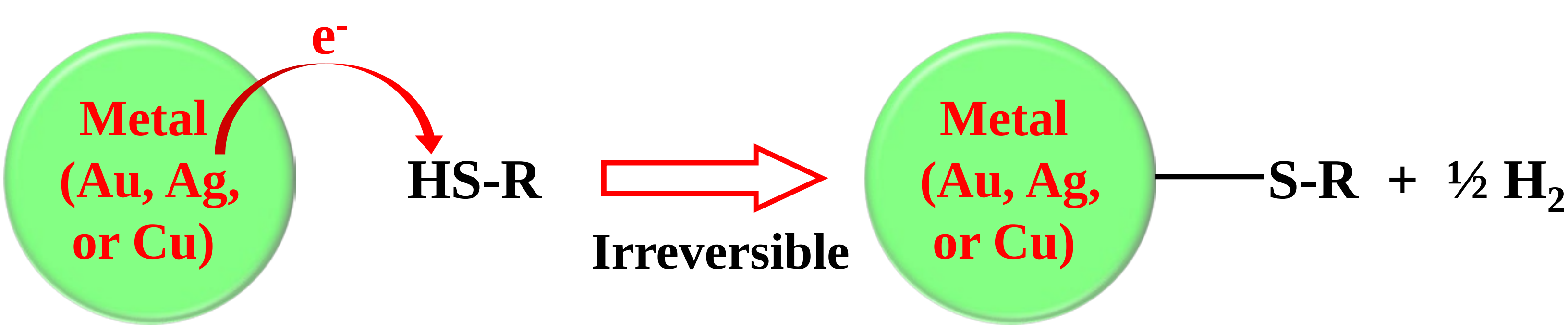
Z907 : 12.2×10^3 $M^{-1}cm^{-1}$

How to adsorb?
Physisorption vs Chemisoprtion



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R \rightleftharpoons H^+ + {}^-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

Le Chatelier's principle



Electrolyte

Consists of

1. Redox couples
   - ✓ I^-/I_3^- , Br^-/Br_3^-
   - ✓ $Se(CN)^-/(Se(CN)_3^-$
   - ✓ $Co(III)/Co(II)(dbbip)_2$
2. Solvent
   - ✓ Acetonitrile, 3-methoxy-propionitrile, ethylene carbonate (EC), Propylene carbonate (PC), or ionic liquids
3. Additives
   - ✓ Guanidium thiocyanate
   - ✓ *t*-butyl pyridine

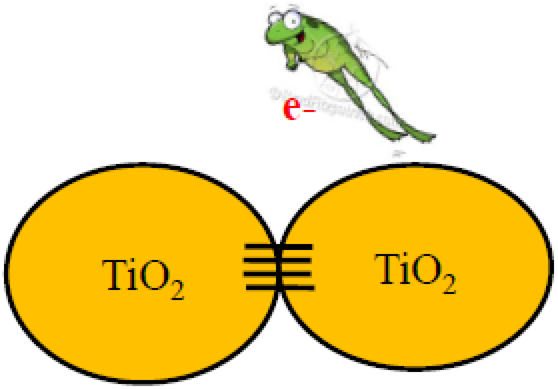
Types

1. Liquid electrolyte
   - ✓ High efficiency (~11 % at 100 mW/cm^2)
   - ✓ Difficulty in preparation and maintenance
   - ✓ Solvent Leakage
   - ✓ Poor mechanical strength
2. Gel electrolyte
   - ✓ High efficiency (~8 % at 100 mW/cm^2)
   - ✓ High ionic conductivity
   - ✓ Solvent vapor permeation
   - ✓ Poor mechanical strength
3. Polymer electrolyte
   - ✓ Low efficiency (~6 % at 100 mW/cm^2)
   - ✓ No liquid solvent use
   - ✓ Good mechanical strength
   - ✓ Low ionic conductivity
   - ✓ Poor contact between electrolyte and dye

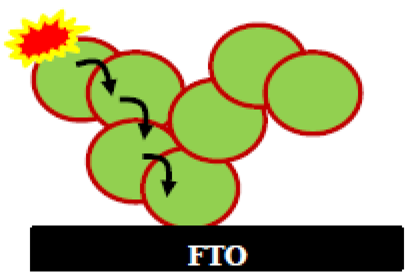
Electron transport of TiO_2 nanoparticles and TiO_2 nanotubes

Charge transport of the photoanode depends,

a. Morphology (particulate, rod, wire, tube etc)
b. Conductivity (semiconductor and conductor)

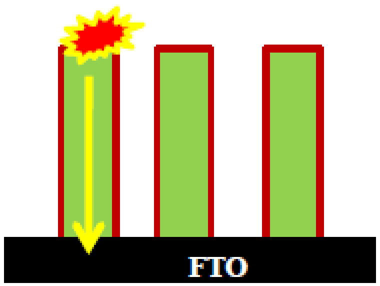


Particulate type material



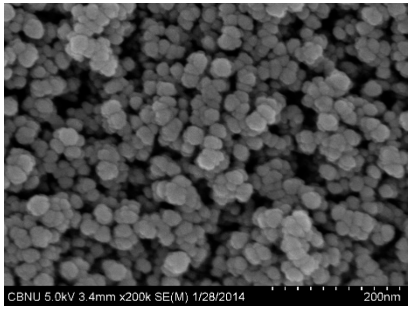
- Hopping conduction
- Grain boundary loss (trapping/detrapping)

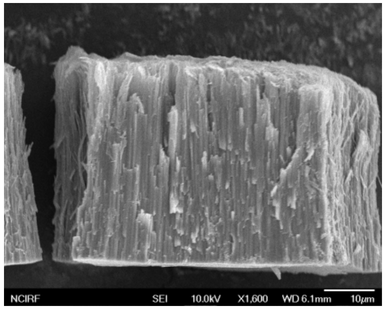
One dimensional material



- Rapid transport
- Reduced grain boundary loss

Nanoparticles vs Nanotubes



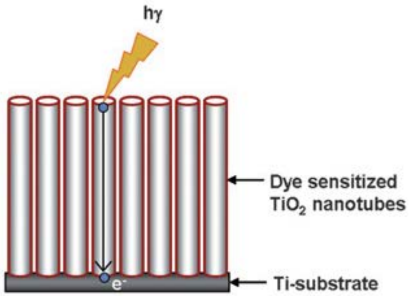


1. Film thickness : 10μm
2. Nanoparticles size : 10-30 nm
3. Porosity : 50-60 %
4. ~600 dye molecules on the TiO_2 NPs' surface

1. Low electron diffusion coefficiency (defects, surface states, grain boundaries etc)
2. Trapped in TiO_2 film about more than 90 % of electrons

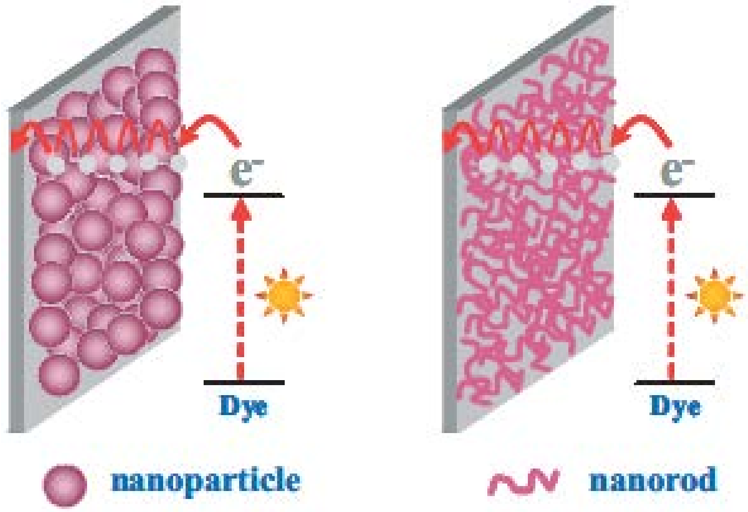
1. High aspect ratio (about 1000 μm)
2. Highly-ordered and vertically-oriented structure
3. Better charge-collection efficiency by faster transport and slower recombination
4. Wild inner diameter : from 100 nm to 25 nm

1. Low surface area
2. Macropores



Nanoscale 2 (2010) 45-59

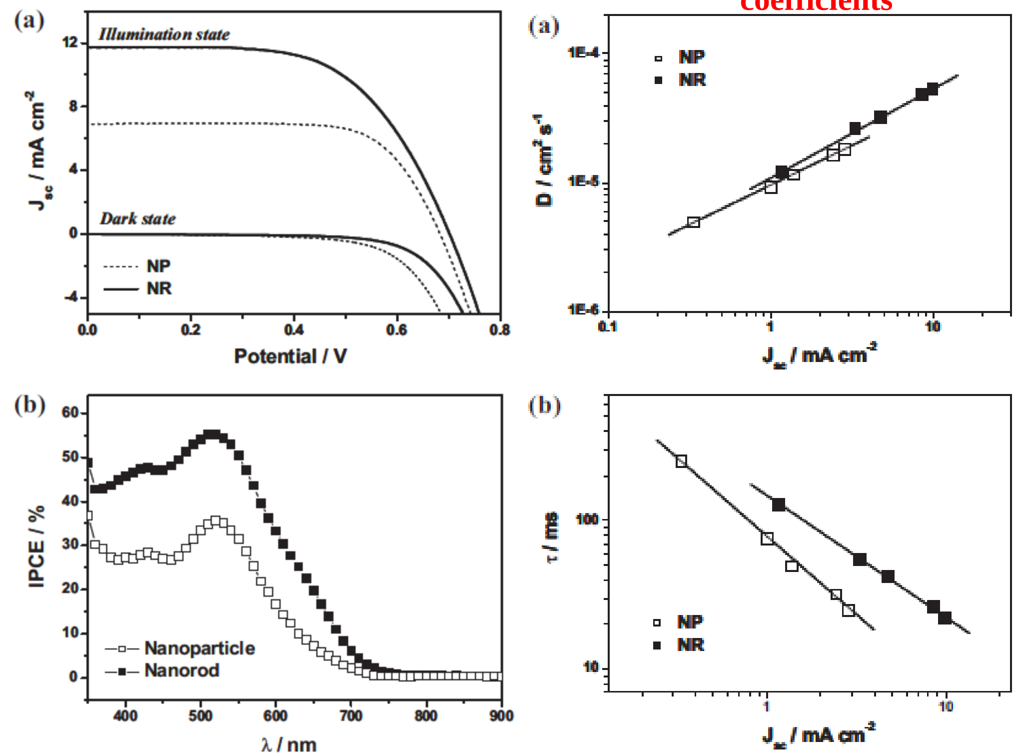
Charge collection efficiency of TiO_2



	TiO_2 nanoparticles	TiO_2 nanorods
Thickness	7.5 µm	7.1 µm
Conversion efficiency	4.3 %	6.2 %

J-V characteristics

Electron diffusion coefficients



IPCE: Incident photon-to-current efficiency

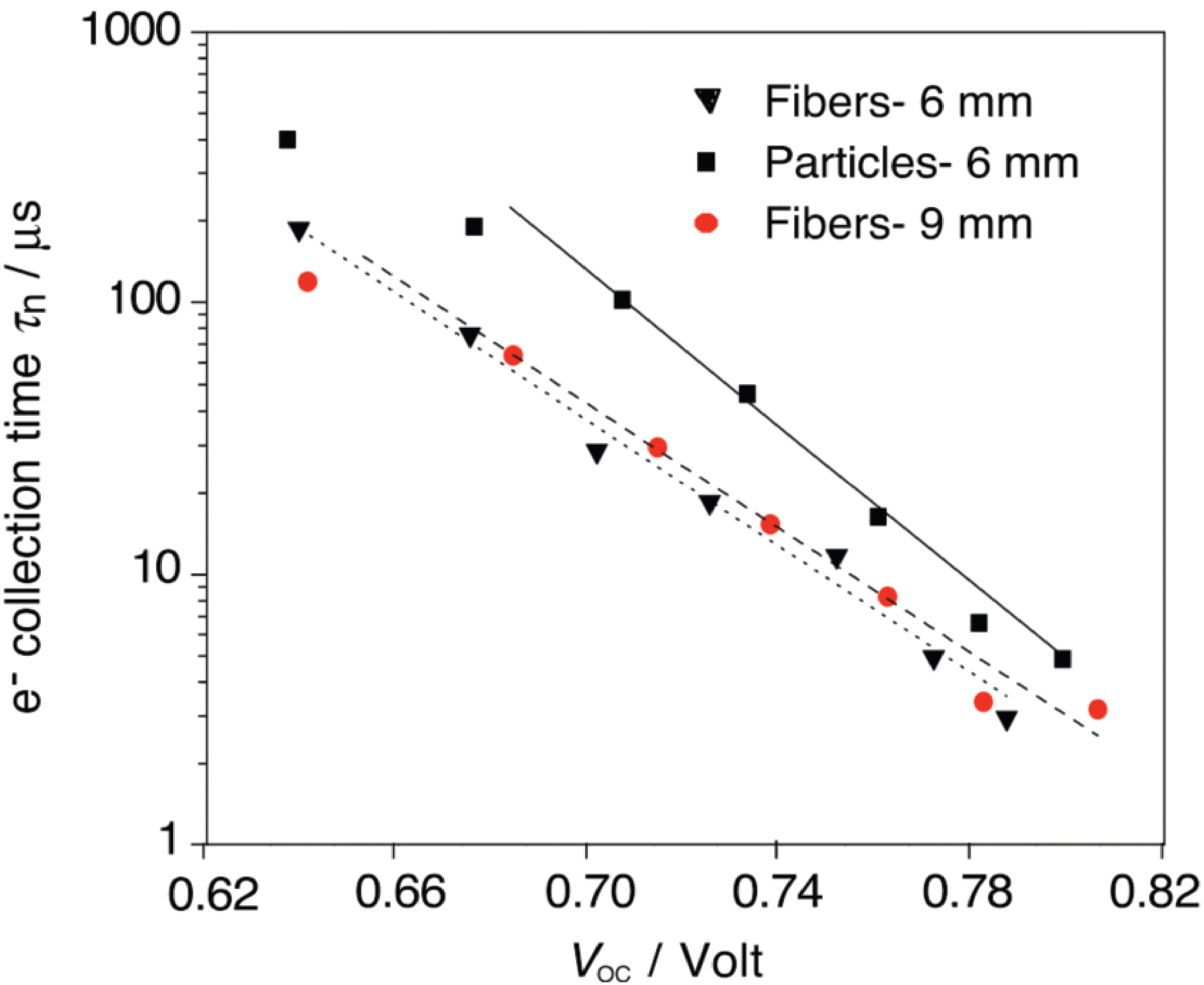
Electron lifetimes

Improvement of energy conversion efficiency

1. Effective electron diffusion coefficiency (electron transport)
2. Improvement of electron lifetimes

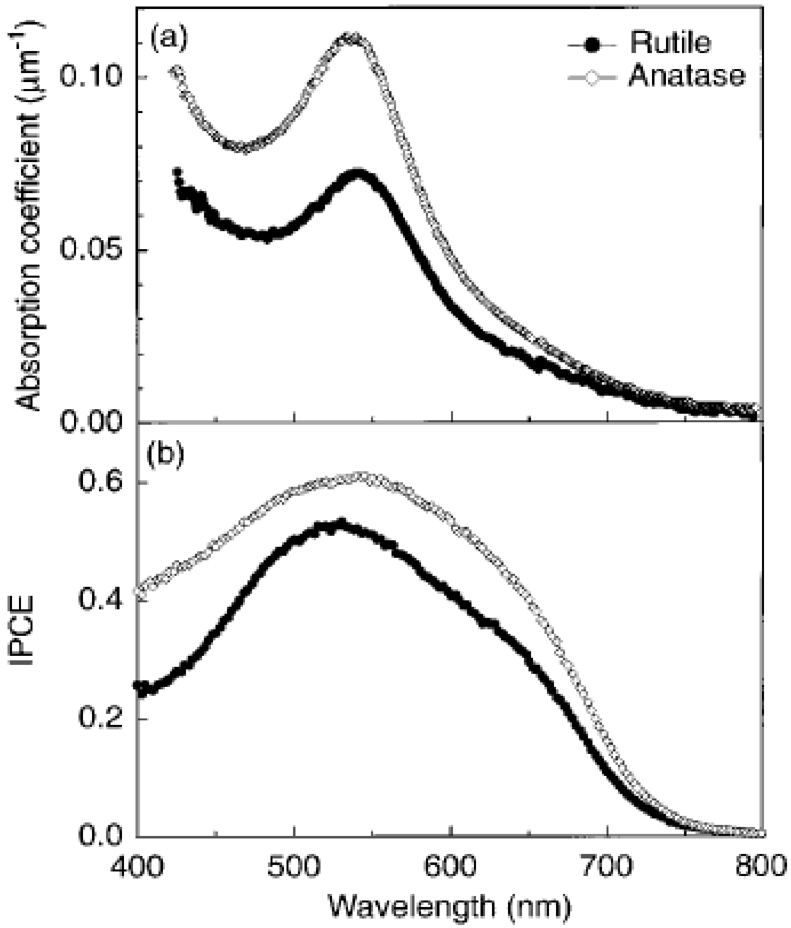
Adv. Mater., 20 (2008) 54-58

Electron transport of TiO_2 nanoparticles vs TiO_2 nanofibers

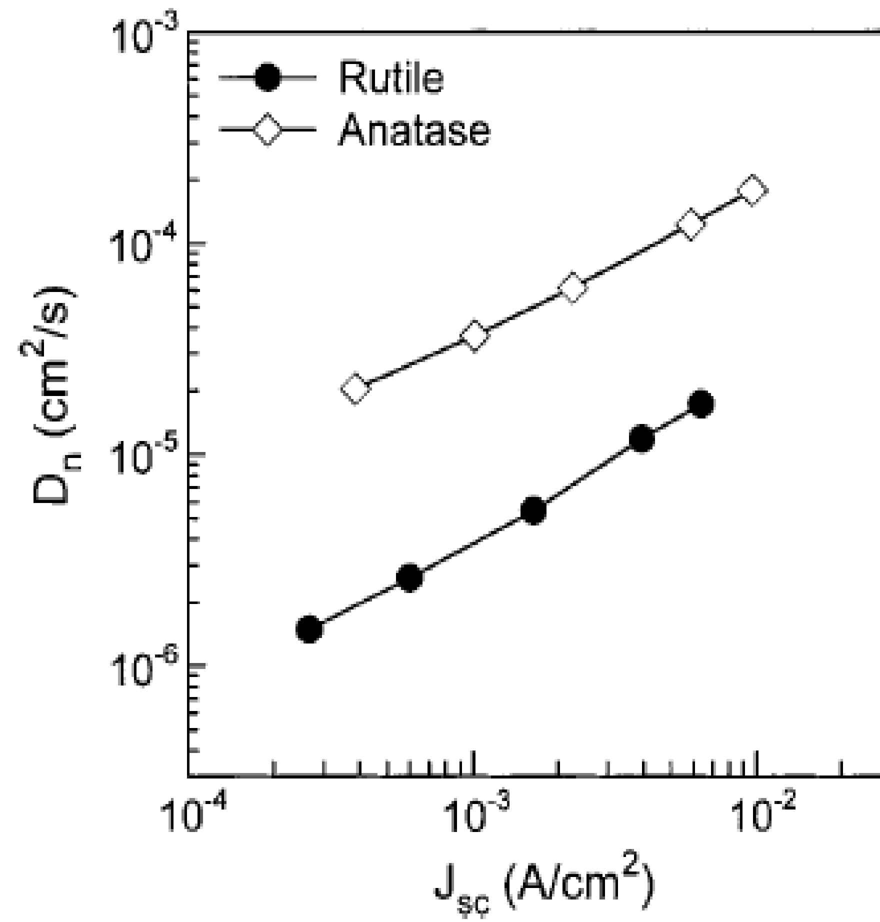


E. Ghadiri. et al, *Nano. Lett.*, **2010,** *10,* 1632

Rutile or Anatase TiO_2 films on DSSCs



IPCE: Incident photon-to-current efficiency

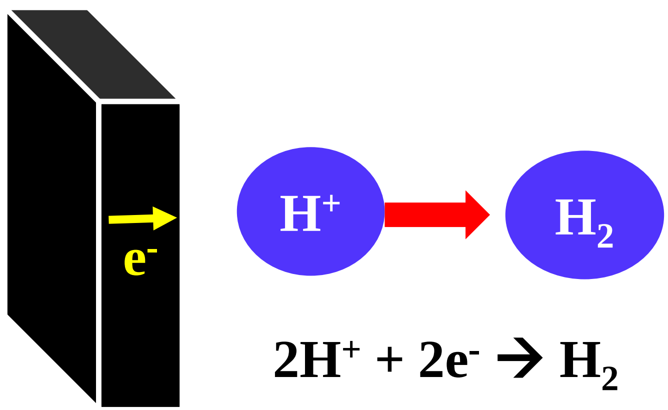


D_n : electron diffusion coefficient

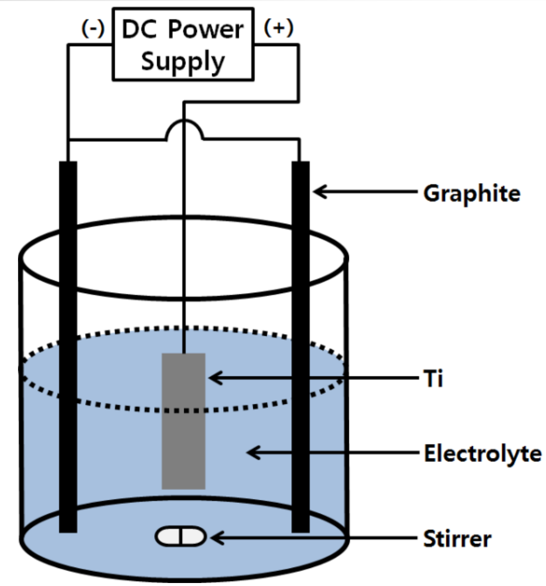
N. G. Park. et al. *J. Phys. Chem. B*, **2000**, *104*, 8989

TiO_2 nanotube arrays by anodization

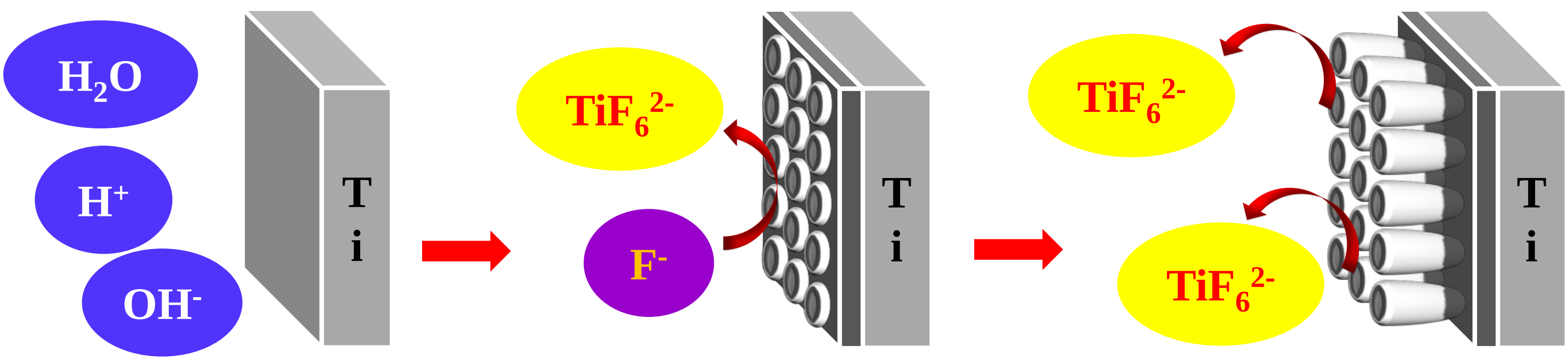
Cathode



$$2H^+ + 2e^- \rightarrow H_2$$



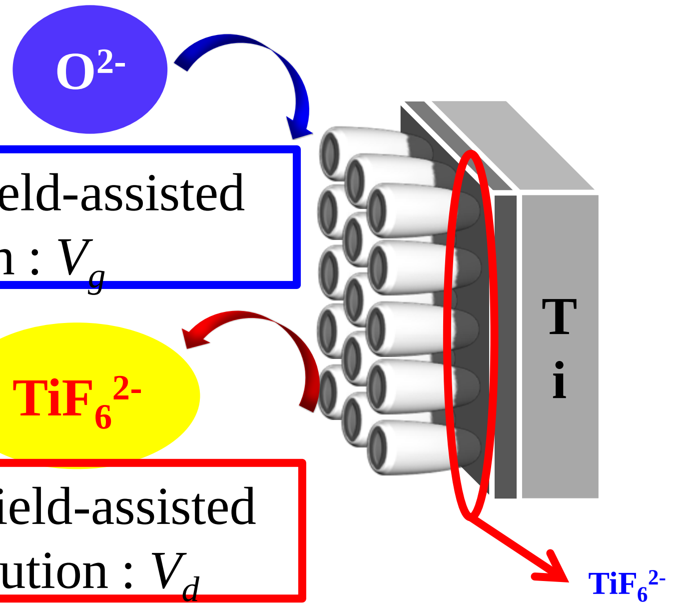
Anode



$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

$$TiO_2 + 6F^- \rightarrow TiF_6^{2-} + 2O^{2-}$$

How to treat TiO_2 nanotube arrays after anodization



enhancing field-assisted oxide growth : V_g

enhancing field-assisted oxide dissolution : V_d

$V_g > V_d$: **long nanotubes**

$V_g < V_d$: **short nanotubes**

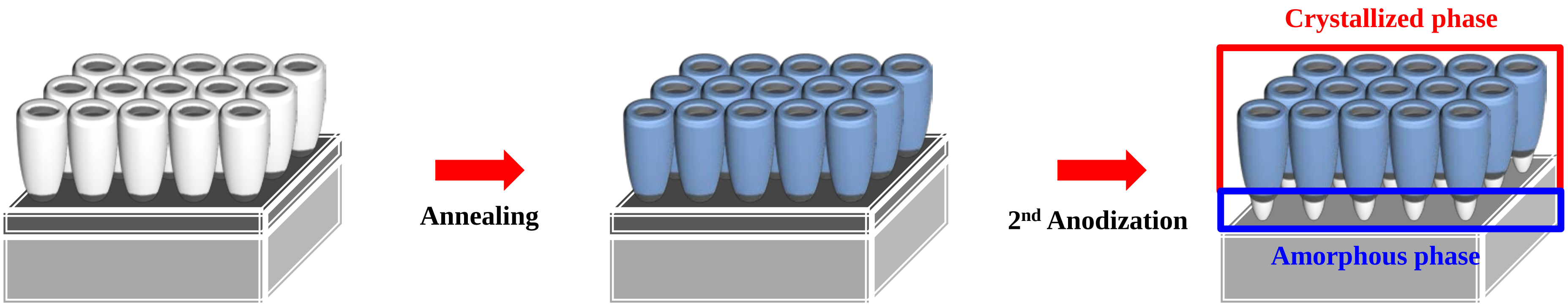
Washed with protic solvent

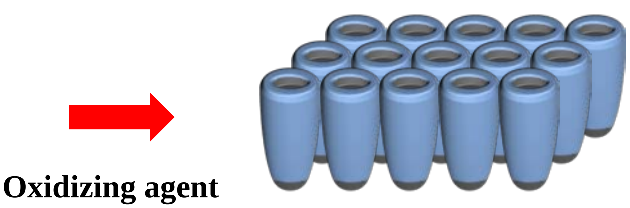
Amorphous phase of freestanding TiO_2 NTs

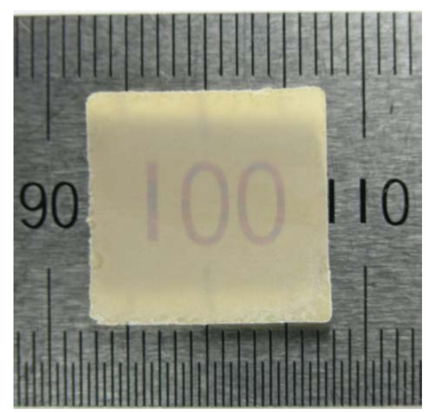
Washed with aprotic solvent

Crystallized phase of freestanding TiO_2 NTs

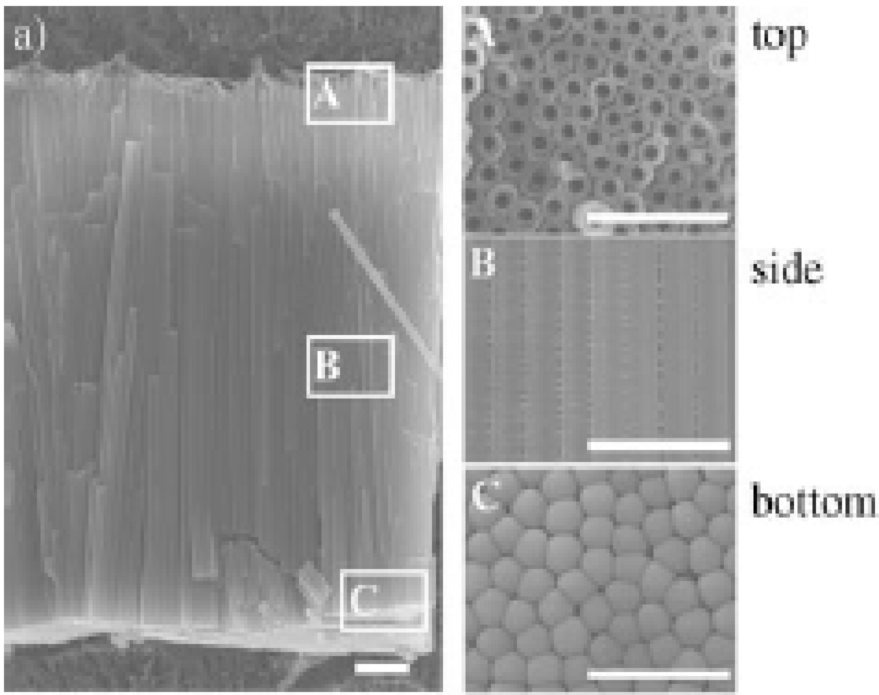
How to prepare freestanding TiO_2 nanotube arrays with crystallized phase

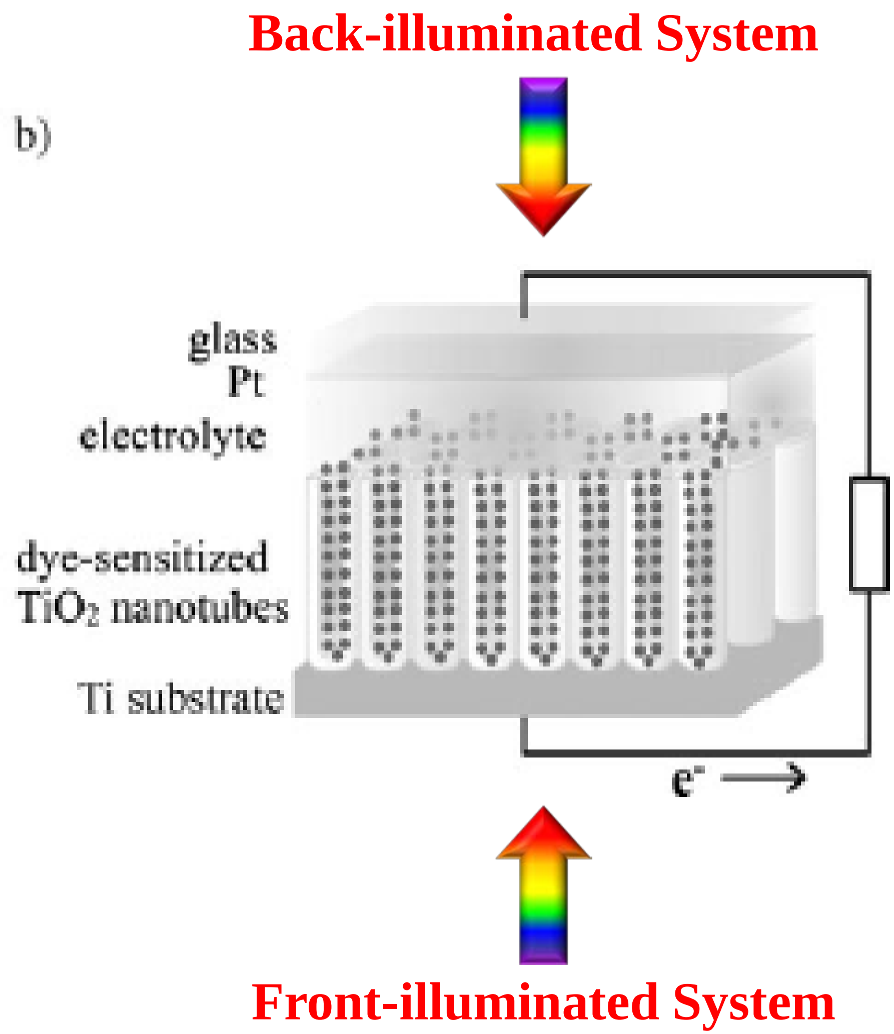






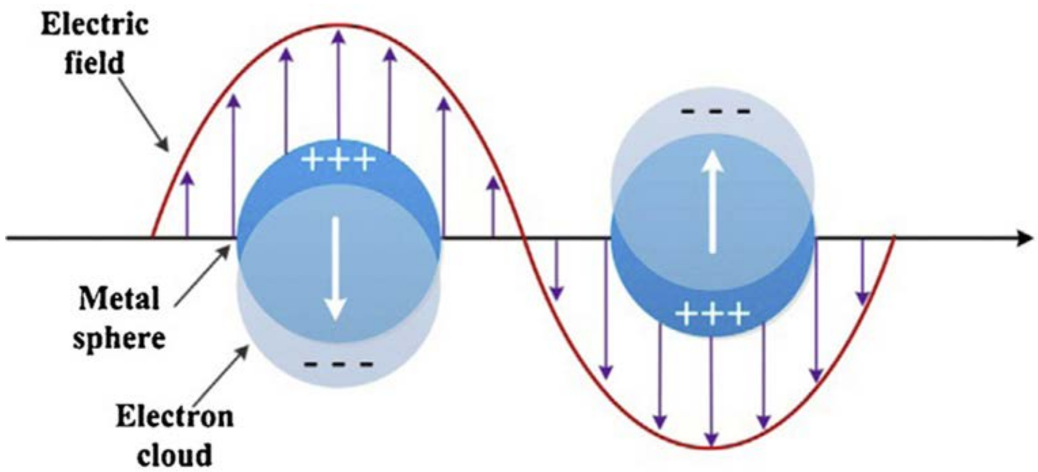
DSSCs based on TiO_2 nanotube arrays





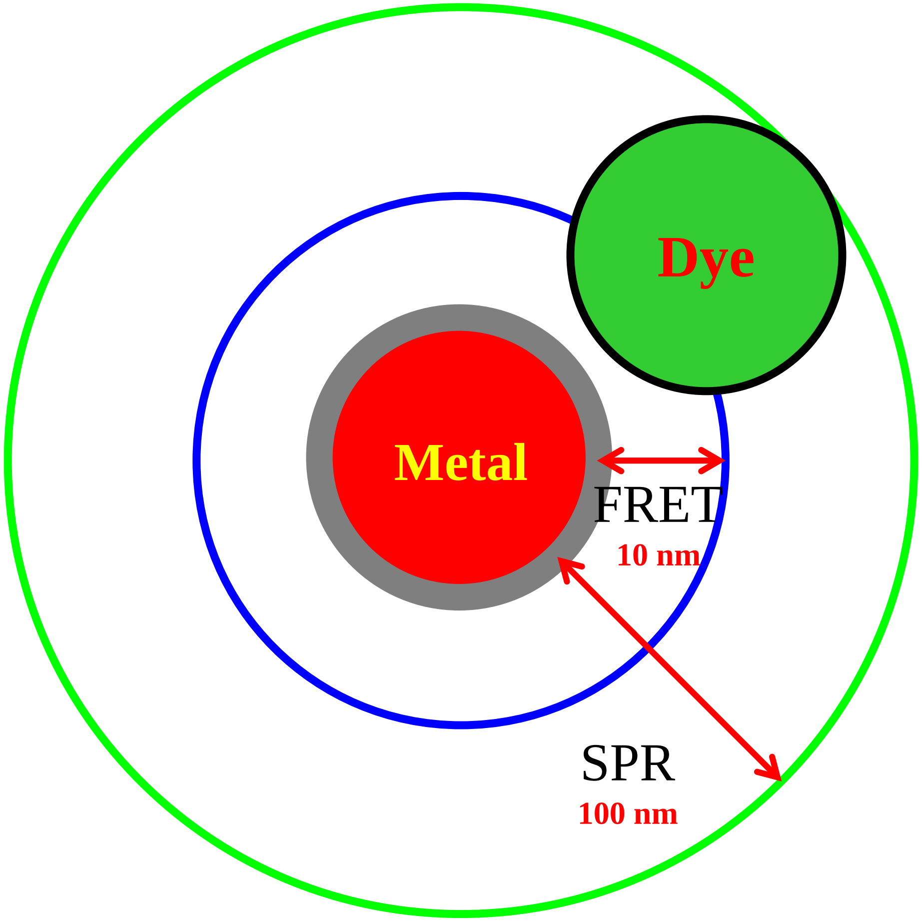
Chem. Asian J. 2009, **4**, 520

Plasmon



- A plasmon is a quantum of plasma oscillation.
- Just as light (an optical oscillation) consists of photons, the plasma oscillation consists of plasmons.
- The plasmon can be considered as a quasiparticle since it arises from the quantization of plasma oscillations, just like phonons are quantizations of mechanical vibrations.
- Plasmons are collective (a discrete number) oscillations of the free electron gas density.
- plasmons can couple with a photon to create another quasiparticle called a plasmon polariton.

SPR vs FRET

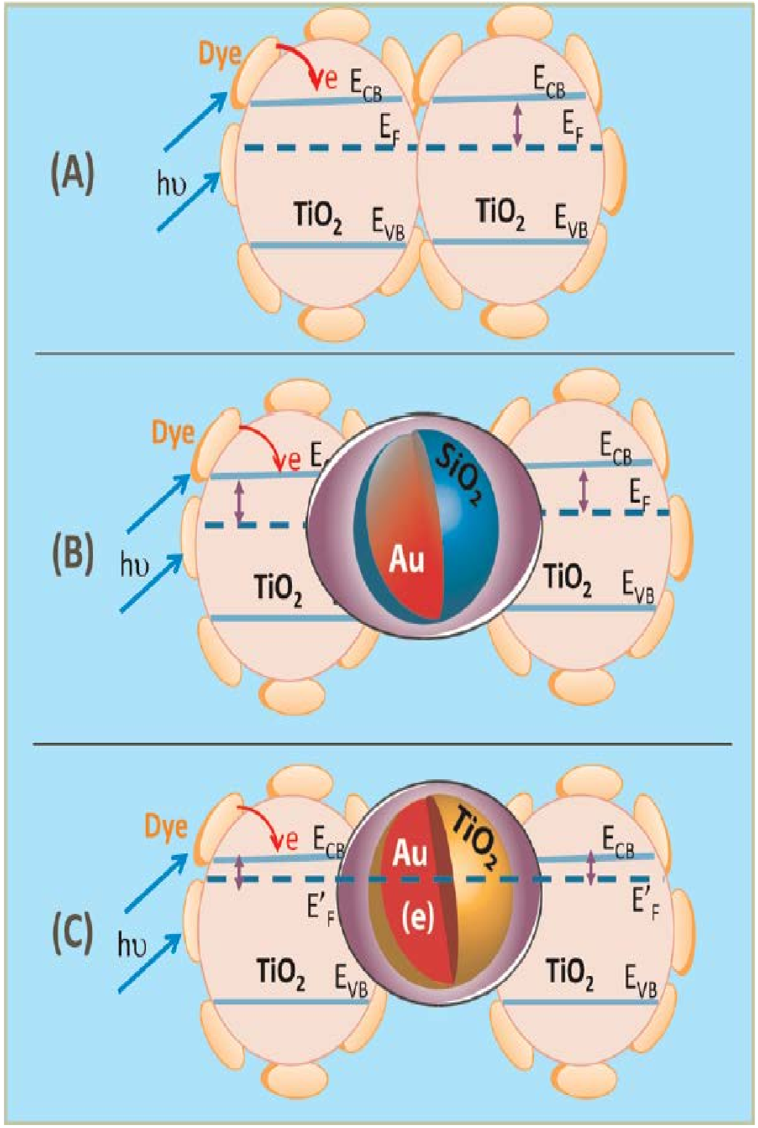


Metal nanoparticles : Au, Ag, Cu, etc.

1. **Electrons are generated by surface plasmon resonance (SPR).**
2. **Electrons are recombined by Förster (or Fluorescence) Resonance Energy Transfer (FRET).**

Metal nanoparticles must be coated with metal oxides.

Charging effect vs Plasmonic effect

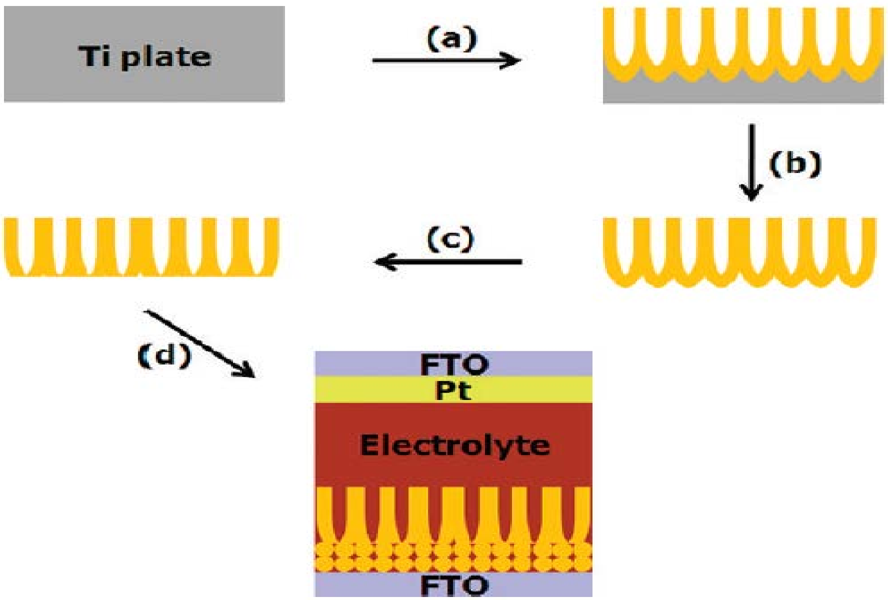


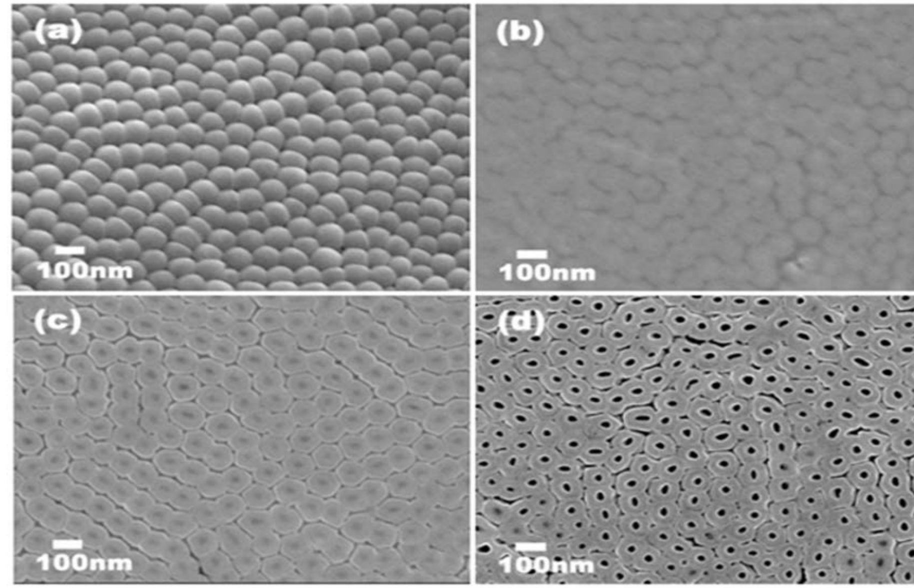
A. TiO_2 NPs
- Acceptor materials.

B. Core@shell type by SiO_2@Au NPs
- Plasmonic effect (SiO_2 is insulator.)
- Better charge separation
- Same Fermi level

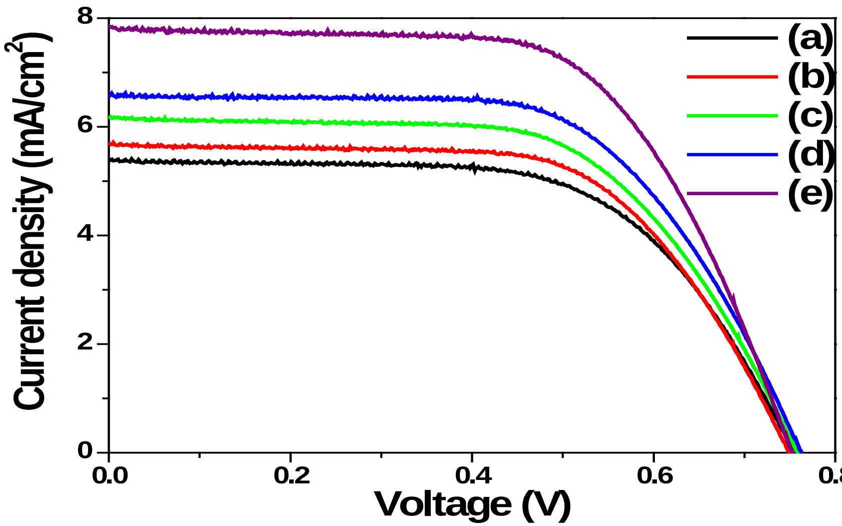
C. Core@shell type by TiO_2 @Au NPs
- Charging effect (TiO_2 is semiconductor)
- Recombination center on active layer
- Increment of electron density
- More negative potential Fermi level
- Increasing Voc

Barrier layer effect on freestanding TiO_2 nanotube arrays





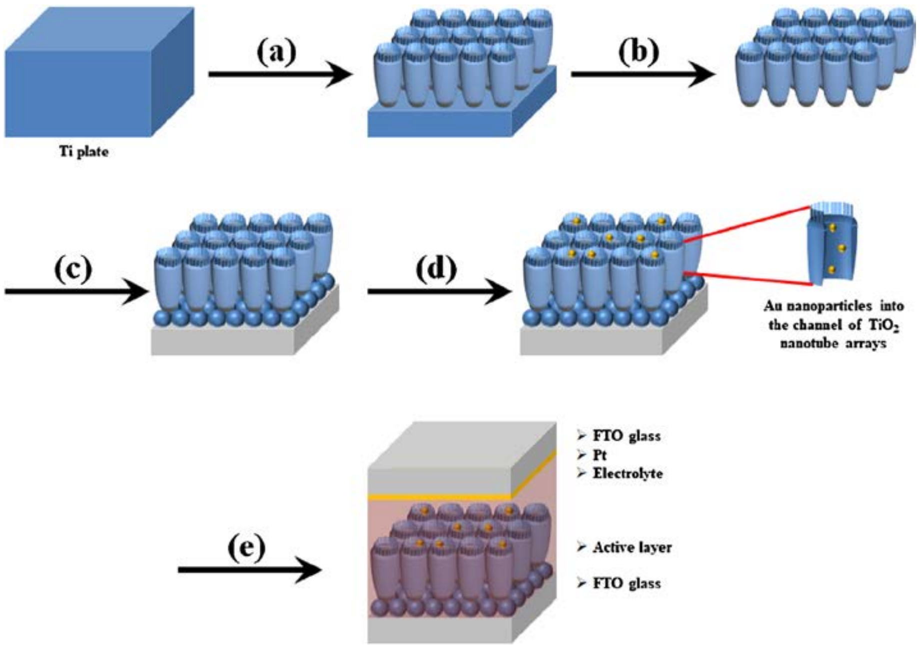
FE-SEM images of bottom layer. After ion milling for (a) 0 , (b) 20 , (c) 30 , and (d) 90 min

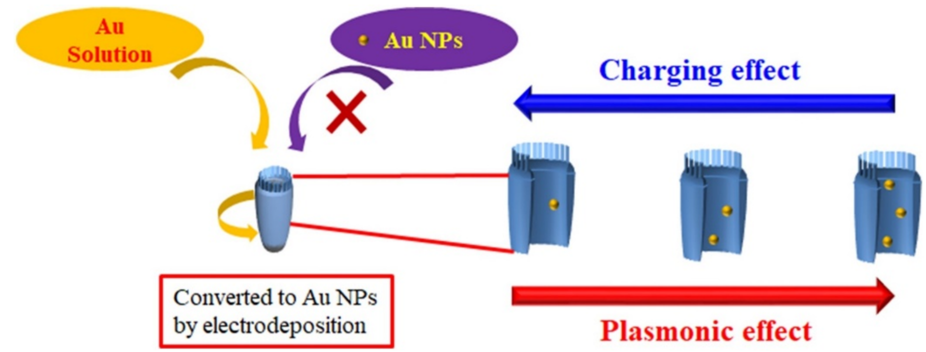


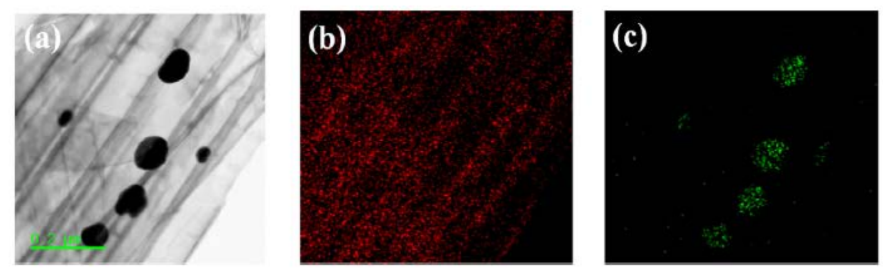
	Ion milling time	J_{sc} (mA/cm²)	V_{oc} (V)	*ff*	η (%)
(a)	0 min	5.37	0.76	0.62	2.5
(b)	10 min	5.69	0.75	0.63	2.7
(c)	20 min	6.17	0.76	0.61	2.9
(d)	30 min	6.59	0.76	0.61	3.1
(e)	90 min	7.85	0.75	0.62	3.7

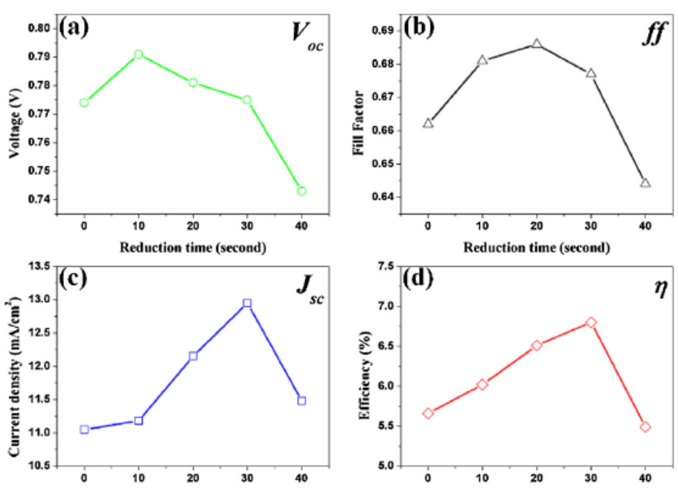
C. Rho, et al., *Journal of Physical Chemistry C* 116(12) (2012) 7213-7218

Charging and Plasmonic effects in DSSCs





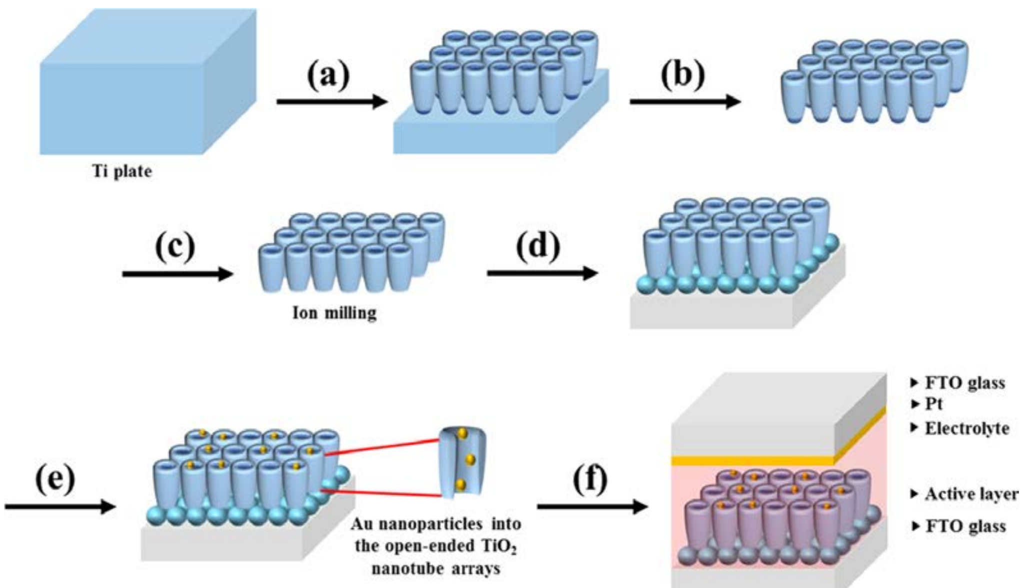


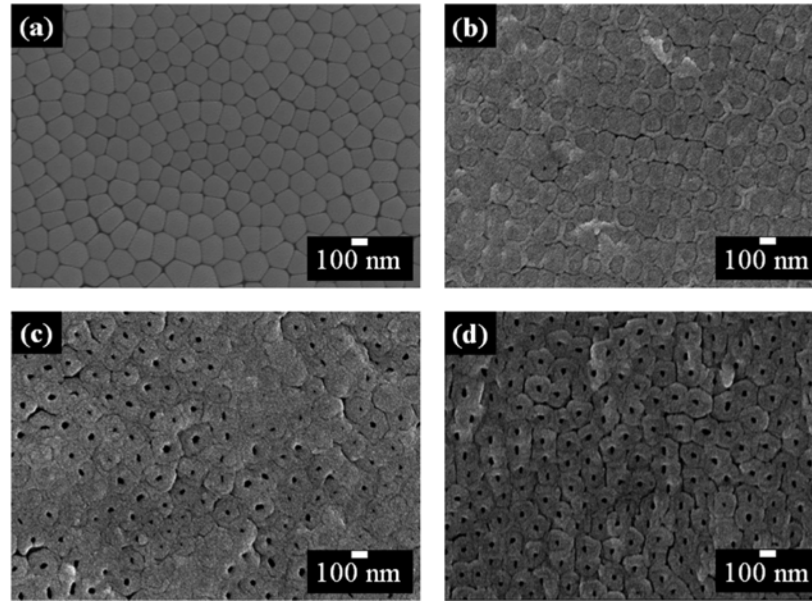


	DSSCs based on the f-TNTAs with Au NPs	J_{sc} (mA/cm^2)	V_{oc} (V)	*ff*	η (%)
(a)	for 0 s	11.05	0.77	0.66	5.66
(b)	for 10 s	11.18	0.79	0.68	6.02
(c)	for 20 s	12.15	0.78	0.69	6.51
(d)	for 30 s	12.95	0.77	0.68	6.80
(e)	for 40 s	11.48	0.74	0.64	5.49

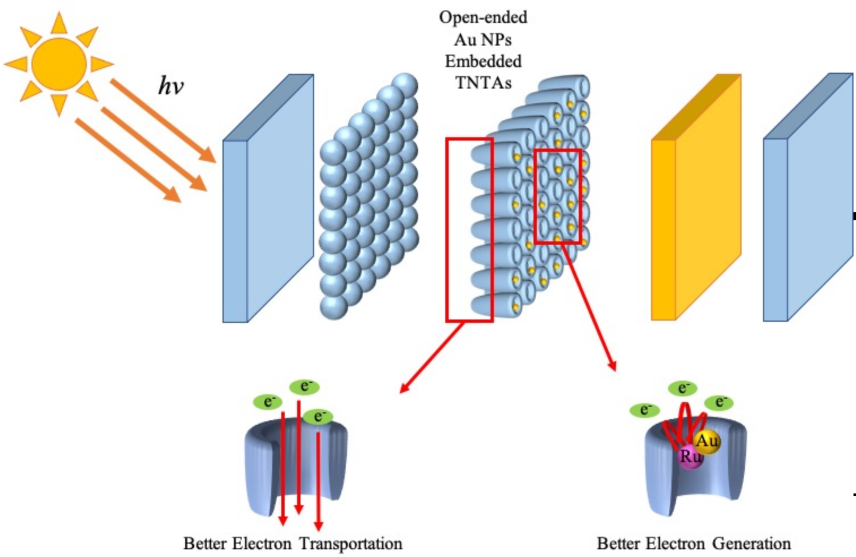
H.-Y. Yang, et al., *Journal of Industrial Engineering Chemistry 80* (2019) 311-317

DSSCs based on the freestanding TiO_2 nanotube arrays with Au NPs





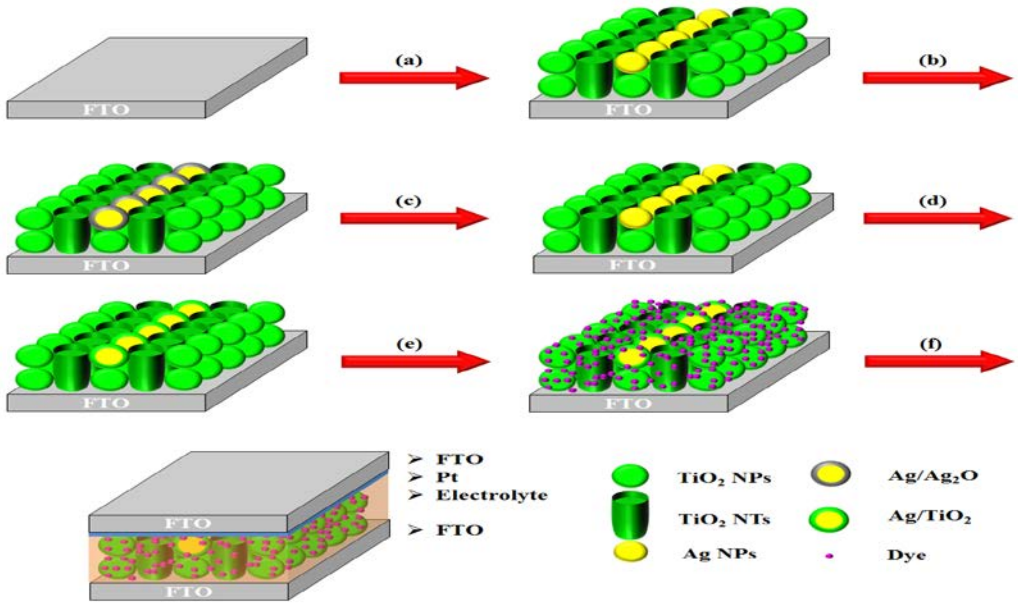
Bottom images of TNTAs by ion milling for (a) 0 min, (b) 30 min, (c) 60 min, and (d) 90 min.

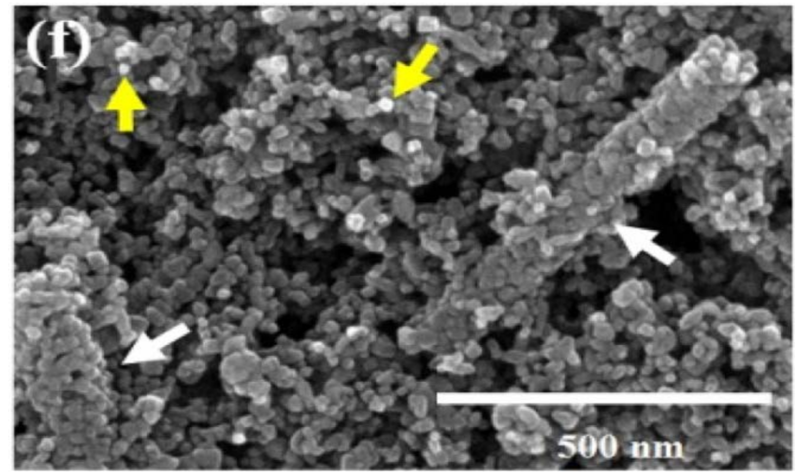


DCCSs based on bottom layer etched TNTAs by ion milling method		J_{sc} (mA/cm^2)	V_{oc} (V)	*ff*	η (%)
(a)	for 10 min	11.83	0.75	0.69	6.12
(b)	for 30 min	12.49	0.77	0.70	6.69
(c)	for 60 min	12.60	0.79	0.70	7.03
(d)	for 90 min	12.72	0.80	0.70	7.12

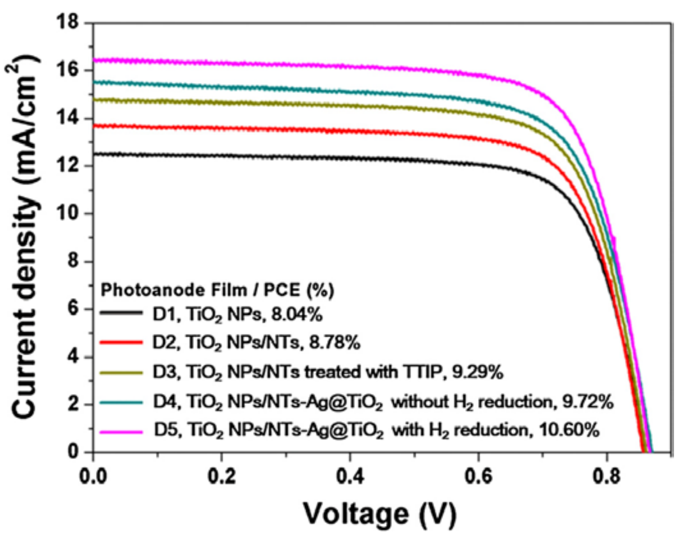
W.-Y. Rho, et al., *ACS OMEGA 4* (2019) 20349-20352

Pre-synthesis Ag nanoparticles on the active layer with TiO_2 nanotubes in DSSCs





TEM image of TiO_2 nanotube arrays with Ag NPs and high-angle annular dark-field (HAADF) image), Yellow dots indicate Ag NPs



	DSSCs based on	J_{sc} (mA/cm^2)	V_{oc} (V)	*ff*	η (%)
D1	TiO_2 NPs	12.46	0.86	0.75	8.04
D2	TiO_2 NPs/NTs	13.62	0.86	0.75	8.78
D3	TiO_2 NPs/NTs treated with TTIP	14.80	0.86	0.73	9.29
D4	TiO_2 NPs/NTs and Ag@TiO_2 without H_2 reduction	15.53	0.87	0.72	9.72
D5	TiO_2 NPs/NTs and Ag@TiO_2 with H_2 reduction	16.46	0.87	0.74	10.60

W.-Y. Rho, et al., *Applied Surface Science* 429 (2018) 23-28

Conclusions

1. **The V_{oc} is increase by charging effect with a small amount of metal NPs incorporated on the active layer because of the more negative Fermi level.**
2. **The J_{sc} is also increased by plasmonic effect with the optimized amount of metal NPs because of better charge separation.**
3. **The V_{oc}, J_{sc}, and *FF* are decreased with large amount of metal NPs because of aggregation.**
4. **The energy conversion efficiency of solar cells is optimized or improved by machine learning and AI**