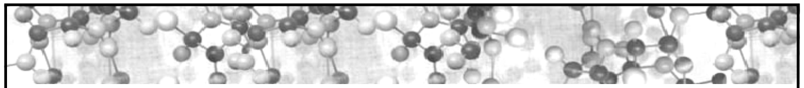


Dye-Sensitized Solar Cells
(www.ardo-portfolio.com)

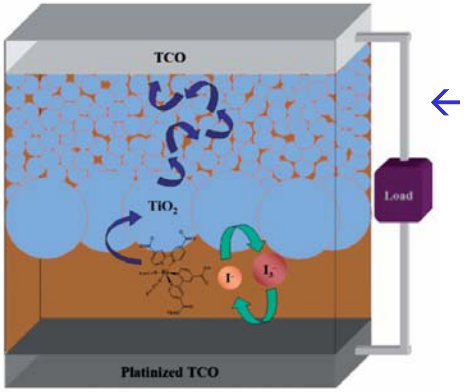
Shane Ardo
chemistry@ardo-portfolio.com
Department of Chemistry

Energy Engineering Course
Tuesday, December 1, 2009

JOHNS HOPKINS UNIVERSITY

Department of Chemistry

Regenerative DSSC Cartoon



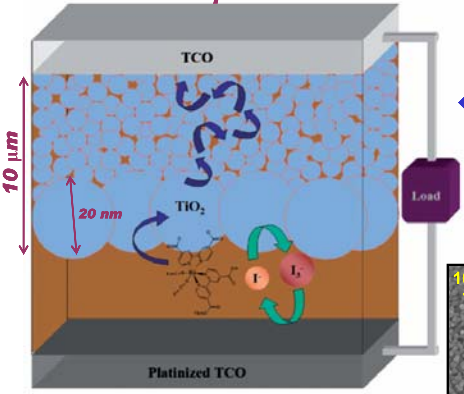
← **Photo-anode**
= light-induced oxidation

Dark Cathode
= light-independent reduction

Energy Environ. Sci. (2008) 1, 66-78 – Hupp & Hamann

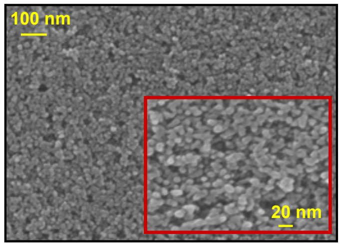
Regenerative DSSC Cartoon

transparent



← **Photo-anode**
= light-induced oxidation

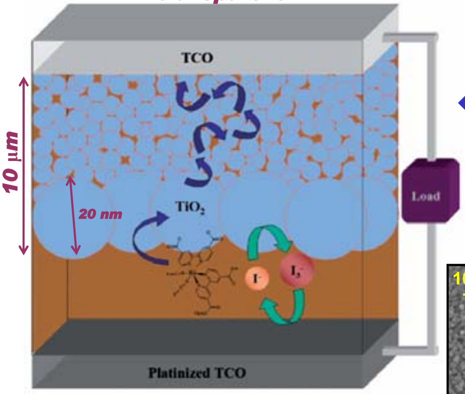
1991 ~50 % porous



Dark Cathode
= light-independent reduction

Regenerative DSSC Cartoon

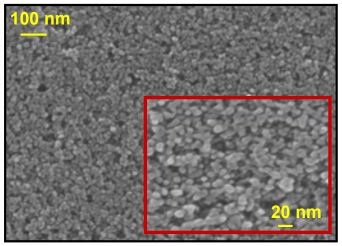
transparent



n-type "Painted" FTO + Light Absorber + Small Cation + p-type Redox Mediator

← **Photo-anode**
= light-induced oxidation

1991 ~50 % porous



Dark Cathode
= light-independent reduction

Show-and-Tell

- TiO_2 Photo-anode on a Glass Slide *(White Background)*
- TiO_2 Photo-anode on a TCO (F-doped SnO_2)
- Dyed Films
  - $Ru(bpy)_3^{2+}$-like
  - Z907
- DSSCs
  - Ours – not sealed
  - O'Regan's – Can I measure a voltage ???
- TiO_2 Sol + Doctor Blading *(= Painting)*
  - Time to make a photo-anode for a DSSC !!!

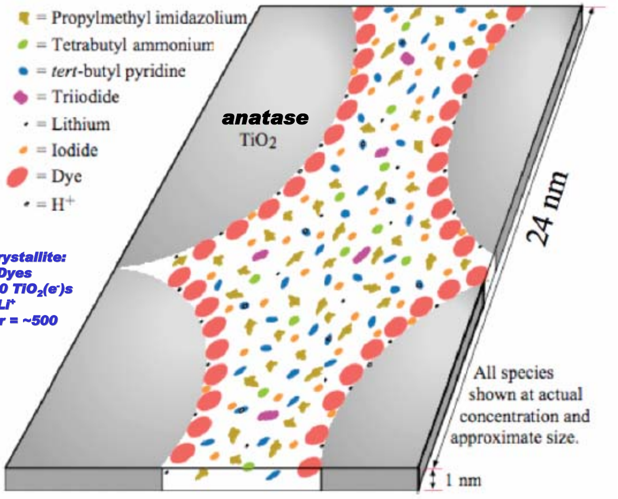
Let's Make a p–n Junction for Comparison

Czochralski Process

Sources: Mainly Department of Energy, Basic Research Needs for Solar Energy Utilization (2005) & NREL, EERE Website

http://www.gcfs.eu/datapool/page/66/cz01.jpg

DSSC Components

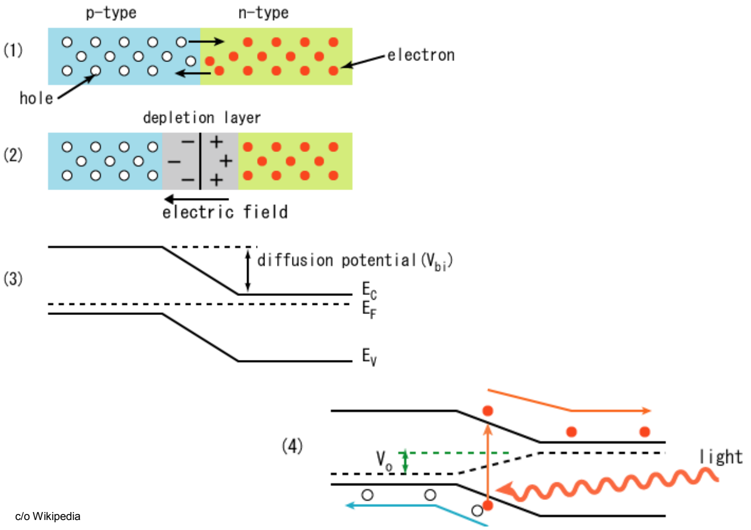


All species shown at actual concentration and approximate size.

Per 20nm Nanocrystallite:
~500 Dyes
~1 – 20 $TiO_2(e^-)$s
~250 Li^+
Roughness factor = ~500

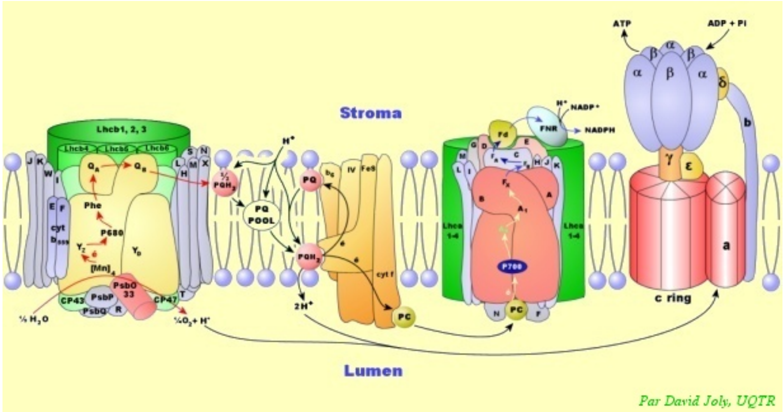
Acc. Chem. Res. (ASAP) – Durrant & O'Regan

Absorption/Charge Separation at a p–n Junction at j_{sc}



c/o Wikipedia

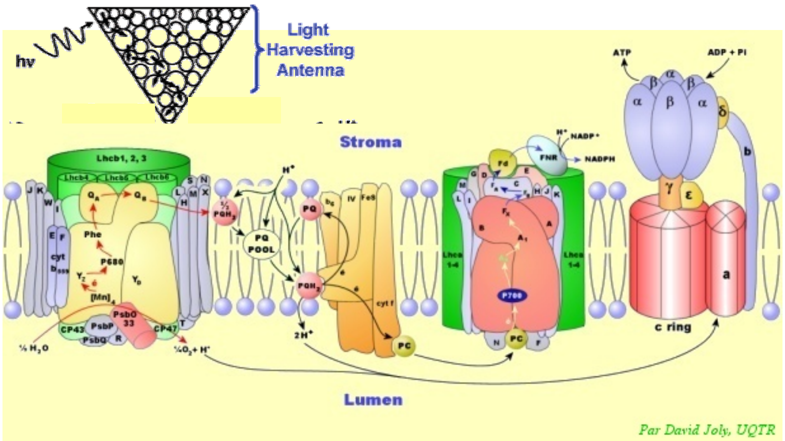
Nature's Photo-induced Charge Separation



Par David Joly, UQTR

c/o Robert Carpentier's website

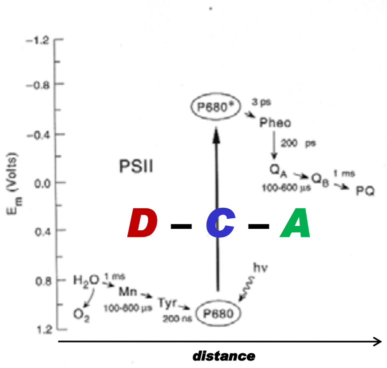
Nature's Photo-induced Charge Separation



Par David Joly, UQTR

Inorg. Chem. (2005) 44, 6802-6827 – Meyer, TJ

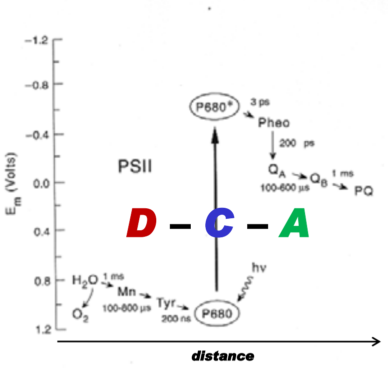
Photosystem II in Plants



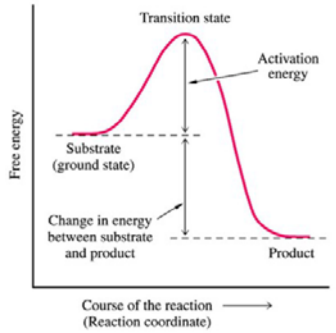
D – C – A

http://www.life.illinois.edu/govindjee/paper/

Photosystem II in Plants



D – C – A

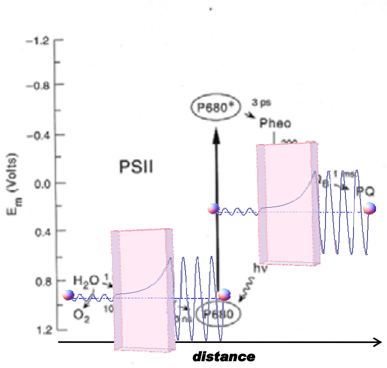


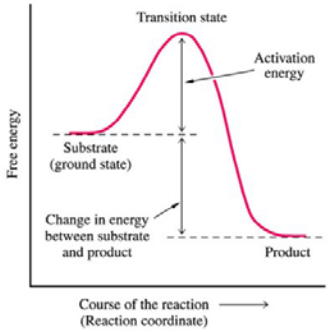
$$k_{\mathrm{ET}} = A \cdot \exp\left[-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right]$$

Arrhenius Equation

http://www4.nau.edu/meteorite/Meteorite/Images/EnergyDiagram.jpg

Photosystem II in Plants



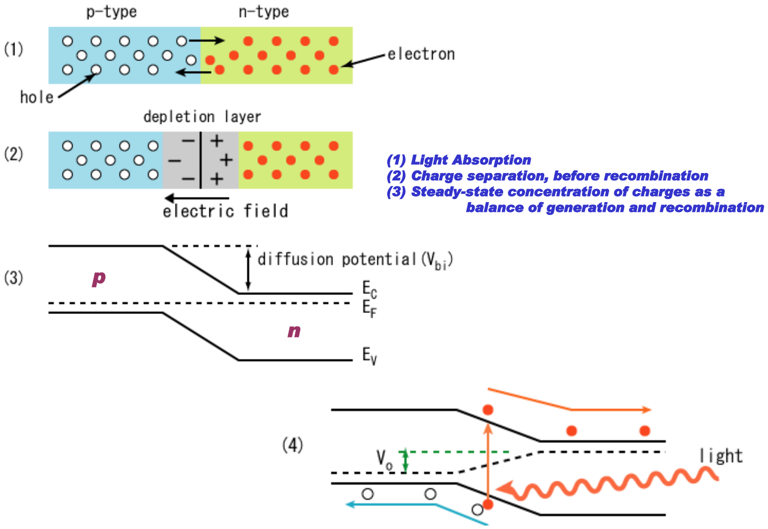


$$k_{\mathrm{ET}} = A \cdot \exp\left[-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right] = A^{'} \cdot \exp[-\beta d] \cdot \exp\left[-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right]$$

Arrhenius Equation ***+ Quantum Mechanical Tunneling Component***

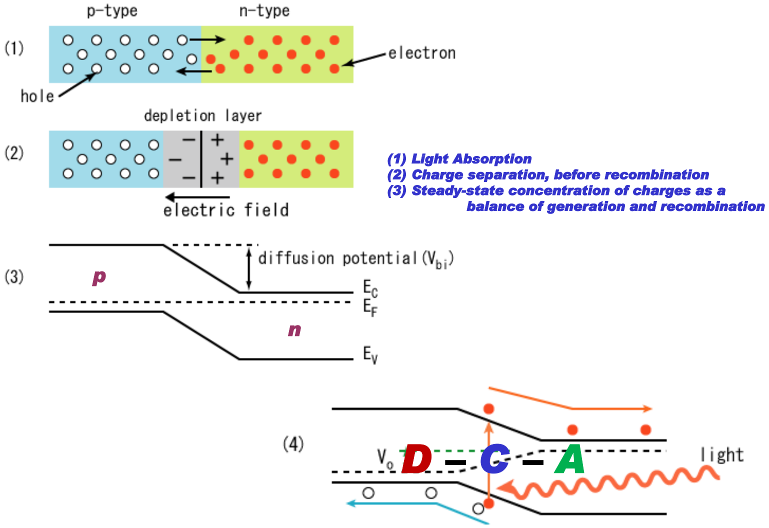
c/o Wikipedia

Recombination in a p–n Junction at V_{oc}



(1) Light Absorption
(2) Charge separation, before recombination
(3) Steady-state concentration of charges as a balance of generation and recombination

Recombination in a p–n Junction at V_{oc}



(1) Light Absorption
(2) Charge separation, before recombination
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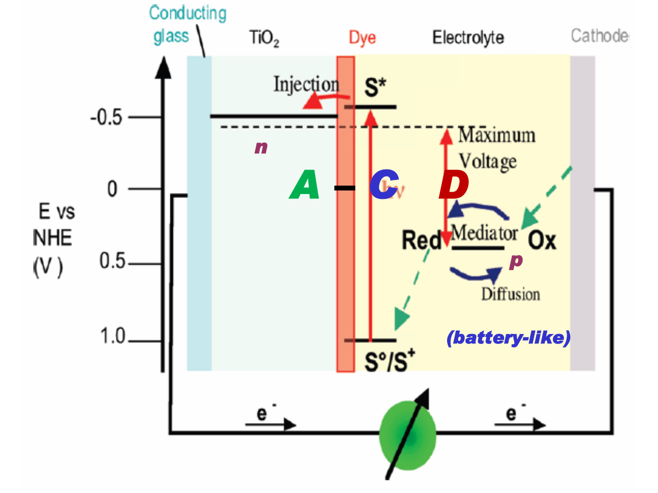
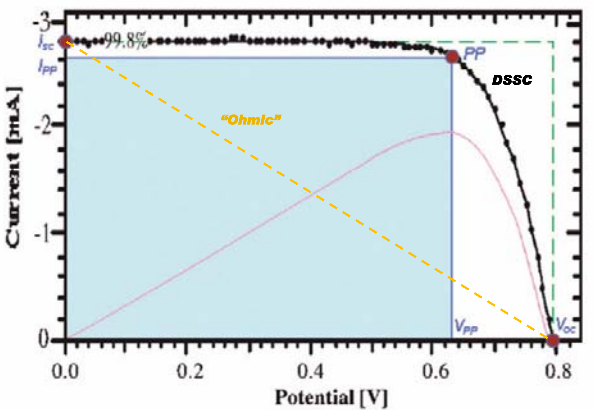
Regenerative DSSC Scheme



Acc. Chem. Res. (ASAP) – Gratzel

(Draw Scheme on Board)

Anatomy of an iV Curve (on board)



$$\eta = \frac{i_{sc} V_{oc} FF}{P_{sun} A_{cell}} = \frac{j_{sc} V_{oc} FF}{P_{sun}}$$

$$FF = \frac{i_{PP} V_{PP}}{i_{sc} V_{oc}}$$

$$\eta_{max(S-Q)} \approx 31\%$$

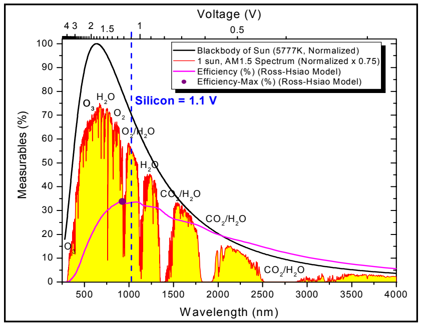
Why not 100% ?

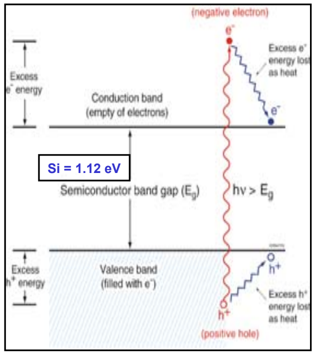
Chem. Soc. Rev. (2008) 38, 115-164 – Meyer & Ardo

Definitions

- η, Light-to-Electrical Power Conversion Efficiency
  - Percentage of power converted (< ~31% for a single-junction cell)
  - (Power Output) / (Power Input)
- Φ, Quantum Yield
  - Percentage (Probability) of the occurrence of an event (≤ 100%)
  - (Rate of Productive Event) / (Sum of the Rates of All Loss Events)

Reasons for Poor Maximum Efficiencies





(1) Transmission of Light with Energy Less than E_{BG} ($\Phi \approx 74$ %)

(2) Thermalization of Electrons with Energy Greater than E_{BG} ($\Phi \approx 67$ %)

(3) Current–Voltage Trade-off (iV curve behavior) ($\Phi \approx 89$ %)

(4) Entropy ($\Phi \approx 64$ %) ***$\Phi_{TOTAL} \approx 74\% \times 67\% \times 89\% \times 64\% \approx 28\%$***

US DOE, Report of the Basic Energy Sciences Workshop on Solar Energy Utilization. In Basic Research Needs for Solar Energy Utilization, Department of Energy: Washington, DC, 2005 (April 18-21), pg. 15.

Definitions

- η, Light-to-Electrical Power Conversion Efficiency
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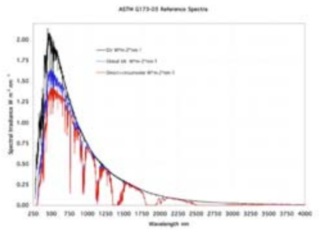
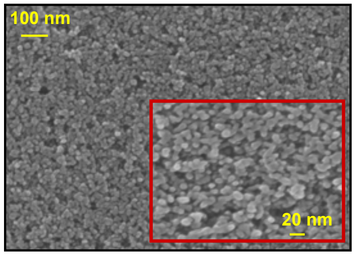
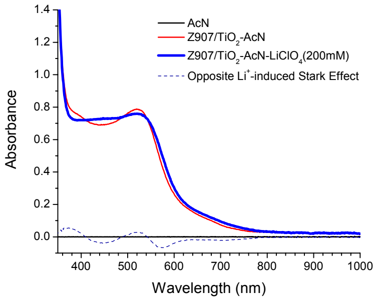
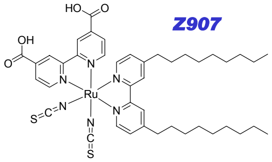
  - (Power Output) / (Power Input)
- Φ, Quantum Yield
  - Percentage (Probability) of the occurrence of an event (≤ 100%)
  - (Rate of Productive Event) / (Sum of the Rates of All Loss Events)
- ε, Extinction Coefficient (Absorption Cross Section; Oscillator Strength)
  - Ability to absorb light on a per molar (concentration), per pathlength basis ($A = \varepsilon c l$)
- ***F***, Faraday's Constant
  - Electronic Charge (*e* or *q*) times Avogadro's number
- **P_{sun}**, 1 sun, Air mass 1.5 Solar Irradiance Spectrum
  - 100 mW/cm^2 (1000 W/m^2) as sunlight in US under typical conditions

Ultraviolet–Visible Absorption Spectra



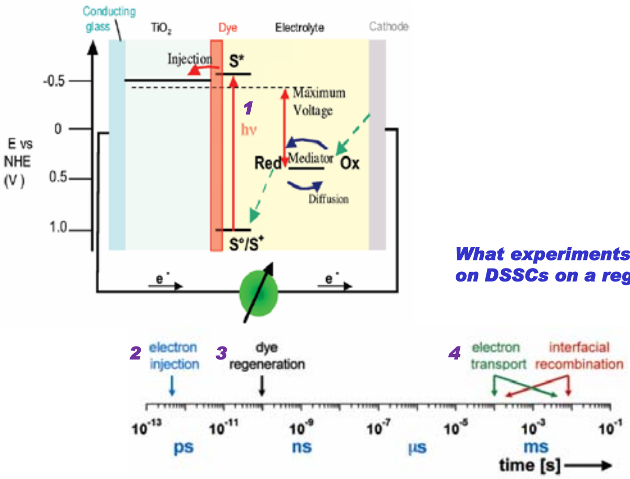






NREL Website

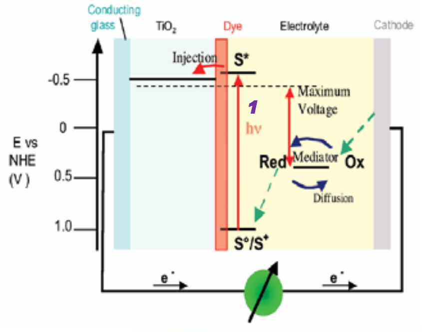
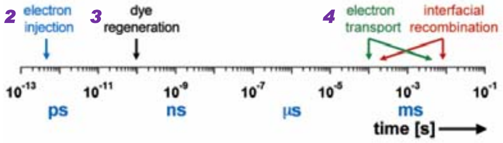
Timescales for Competing Reactions at j_{sc}

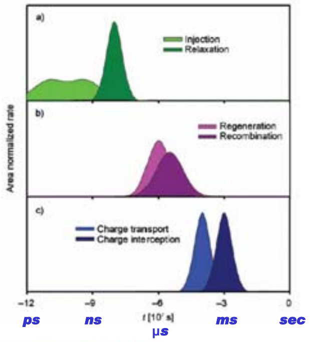


What experiments do I perform on DSSCs on a regular basis ?

Inorg. Chem. (2005) 44, 6841-6851 – Gratzel

Timescales for Competing Reactions at MPP

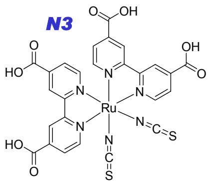



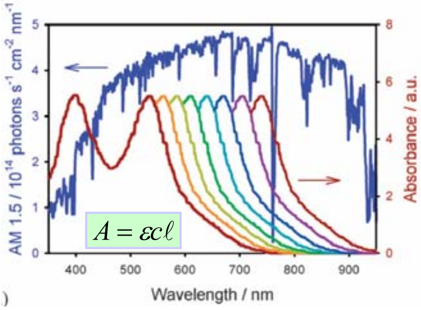


Chem. Eur. J. (2008) 14, 4458-4467 – Hupp & Hamann

Current Density

Ultraviolet–Visible Absorption Spectra





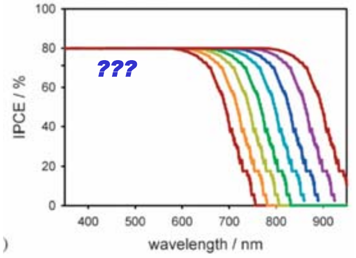
$A = \varepsilon c \ell$

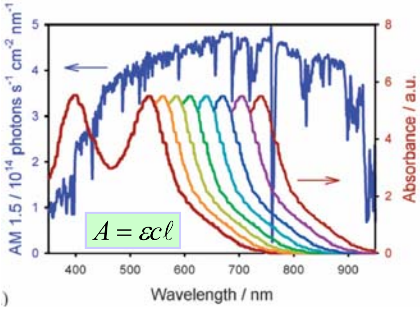
Beer–Lambert Law

Energy Environ. Sci. (2008) 1, 66-78 – Hupp & Hamann

Ultraviolet–Visible Absorption Spectra

$$IPCE(\lambda) = \phi_{\text{abs}} \cdot \phi_{\text{inj}} \cdot \phi_{\text{coll}}$$





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Energy Environ. Sci. (2008) 1, 66-78 – Hupp & Hamann

Ultraviolet–Visible Absorption Spectra

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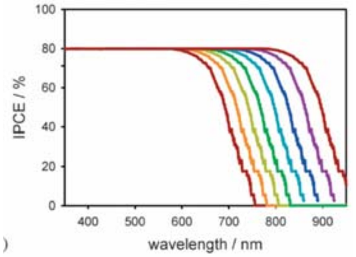
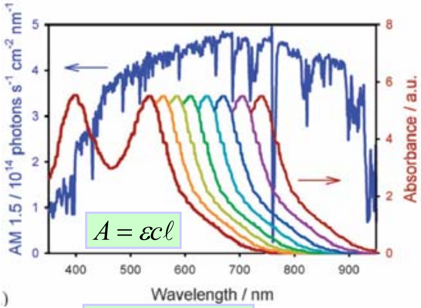




$A = \varepsilon c \ell$

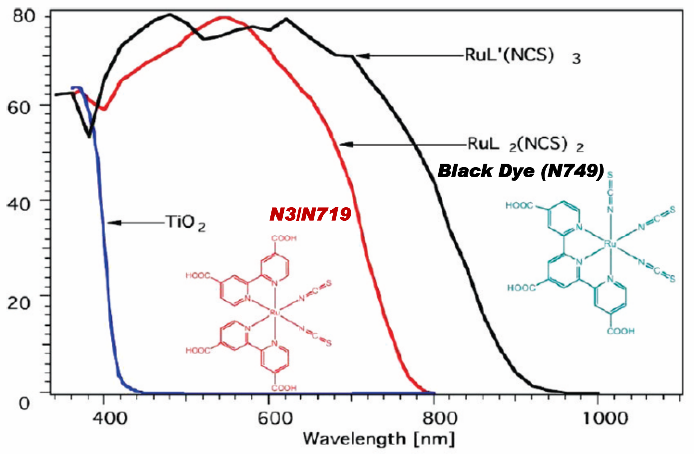
$$A = -\log[\%T]$$

$$\alpha(\lambda) = \phi_{\text{abs}}(\lambda) = \frac{\text{number absorbed}}{\text{number incident photons}}$$

$$= 1 - \%T = 1 - 10^{-Abs} = 1 - 10^{-\varepsilon c \ell}$$

Absorbance (A)	Absorptance (α, %)
0.1	20.6
0.5	68.4
1.0	90
2.0	99
3.0	99.9

Photocurrent Action Spectra



Acc. Chem. Res. (ASAP) – Gratzel

The Photocurrent Action Spectrum

$$IPCE(\lambda) = \phi_{\mathrm{abs}} \cdot \phi_{\mathrm{inj}} \cdot \phi_{\mathrm{coll}} = \alpha(\lambda) \cdot APCE(\lambda)$$

$$\alpha(\lambda) = \phi_{\mathrm{abs}}(\lambda) = \frac{\text{number absorbed}}{\text{number incident photons}} = 1 - \%T = 1 - 10^{-Abs} = 1 - 10^{-\varepsilon c \ell}$$

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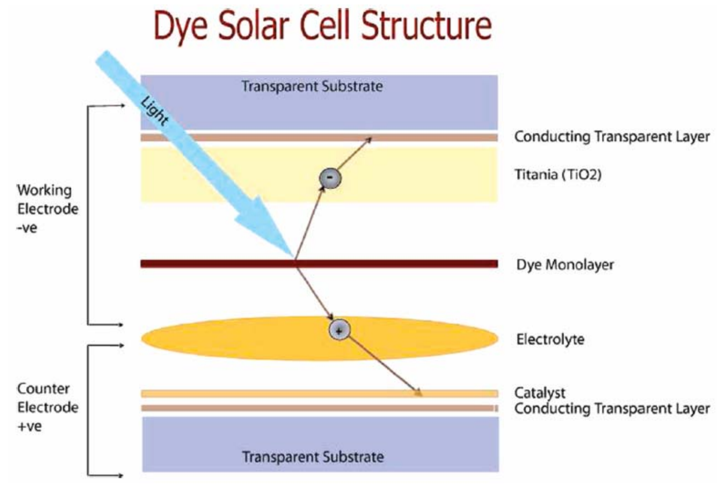
$$\phi_{\mathrm{inj}}(\lambda) = \frac{\text{number injected}}{\text{number excited}} = \frac{\text{Rate of Injection}}{\text{Rates of Loss}} = \frac{k_{\mathrm{inj}}[S^*]}{k_{\mathrm{r}}[S^*] + k_{\mathrm{nr}}[S^*] + k_{\mathrm{inj}}[S^*]} = \frac{k_{\mathrm{inj}}}{k_{\mathrm{r}} + k_{\mathrm{nr}} + k_{\mathrm{inj}}}$$

Initial Charge Separation (Φ_{inj})



Acc. Chem. Res. (ASAP) – Gratzel

The Photocurrent Action Spectrum

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$$\alpha(\lambda) = \phi_{\mathrm{abs}}(\lambda) = \frac{\text{number absorbed}}{\text{number incident photons}} = 1 - \%T = 1 - 10^{-Abs} = 1 - 10^{-\varepsilon c \ell}$$

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$$\eta_{\mathrm{coll}} = \phi_{\mathrm{coll}} = \frac{\text{number as current}}{\text{number injected}} = \frac{\text{Flux of Current}}{\text{Rates of Loss}}$$

Difficult to Quantify, except backwards

The Photocurrent Action Spectrum

$$IPCE(\lambda) = \phi_{\text{abs}} \cdot \phi_{\text{inj}} \cdot \phi_{\text{coll}} = \alpha(\lambda) \cdot APCE(\lambda)$$

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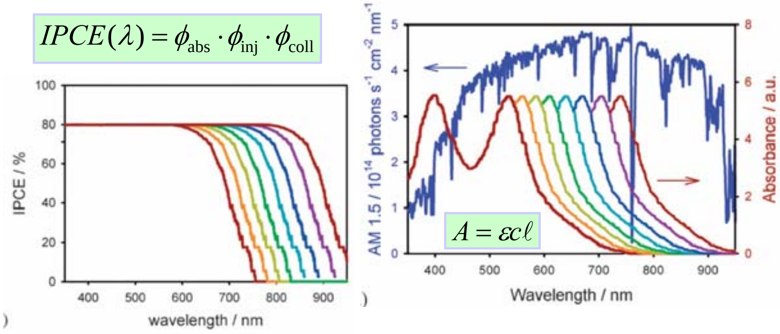
$$\cancel{\eta_{\text{coll}}} = \phi_{\text{coll}} = \frac{\text{number as current}}{\text{number injected}} = \frac{\text{Flux of Current}}{\text{Rates of Loss}}$$

Difficult to Quantify, except backwards

Near-Ideal Short-Circuit Current Density

$$IPCE(\lambda) = \phi_{\text{abs}} \cdot \phi_{\text{inj}} \cdot \phi_{\text{coll}}$$



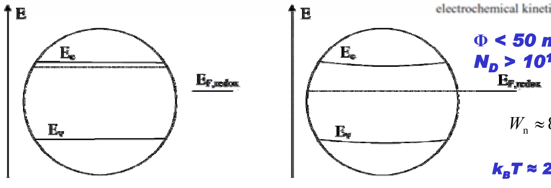
$$j_{\text{sc}} = \int_0^{\infty} e \cdot IPCE(\lambda) \cdot I_{\text{sun}}(\lambda)\, d\lambda$$

Absorbance (A)	Absorptance (α, %)
0.1	20.6
0.5	68.4
1.0	90
2.0	99
3.0	99.9

p–n Junctions vs. other cells

TABLE 1: Summary of Photovoltaic Cell Configurations

phenomenon→ ↓type of solar cell↓	light absorbed by[a]	type of mobile charges in device[b]	contact selectivity for charge carriers	current mechanism
p/n junction ***N_D ~ 10^{16} cm^{-3}***	semiconductor	electronic	electric field ***ε_o ~ 12***	drift; some diffusion possible
point contact	semiconductor	electronic (+ ionic, for pec variant)[c]	electric field due to contacts	diffusion[c] (electronic charge carriers); diffusion for ions (drift near the contacts)
photogalvanic	dye	ionic	electrochemical kinetics	ion diffusion
photoelectrochemical (PEC)	semiconductor	electronic and ionic	electric field and electrochemical kinetics	ion diffusion and electronic charge carrier drift
nanoporous photoelectrochemical (PEC)	semiconductor	electronic and ionic	electrochemical kinetics	diffusion
organic	semiconductor	electronic (e.g., via excitons)	nature of organic material and/or its interface with the contacts	can be diffusion or drift, depending on cell type
surface-sensitized Schottky barrier	dye	electronic	ballistic, electric field	ballistic and drift
dye-sensitized (DSSC)	dye	electronic and ionic	energy level (mis)match between molecules and semiconductor; electrochemical kinetics	diffusion



Before contact

After contact

Φ < 50 meV unless N_D > 10^{18} cm^{-3}

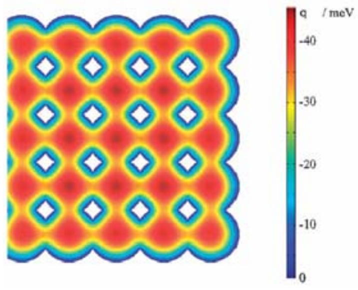
$$W_{\text{n}} \approx 8L^{\text{n}}_{\text{Debye}} = 8\sqrt{\frac{\varepsilon_{\text{o}}\varepsilon_{\text{s}}k_{\text{B}}T}{\text{e}^2 N_{\text{D}}}} = C\sqrt{\frac{\varepsilon_{\text{s}}}{N_{\text{D}}}}$$

k_BT ≈ 26 meV at RT

J. Phys. Chem. B (2004) 108, 8016-8022 – Bisquert, Zaban, Hodes, Cahen, Ruhle and Phys. Chem. Chem. Phys. (2007) 9, 2630-2642 – Peter

(Draw Potential Drop Scenario on Board)

DSSC Small Internal Electric Field



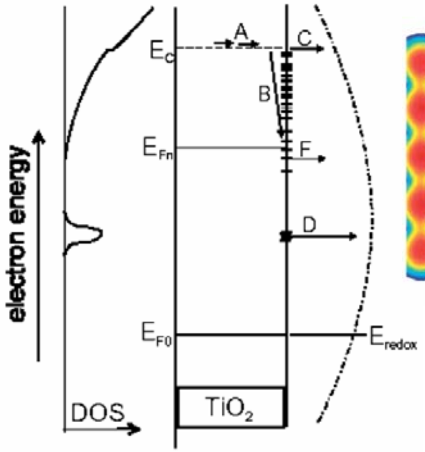
$$W_{\text{n}} \approx 8L^{\text{n}}_{\text{Debye}} = 8\sqrt{\frac{\varepsilon_{\text{o}}\varepsilon_{\text{s}}k_{\text{B}}T}{\text{e}^2 N_{\text{D}}}} = C\sqrt{\frac{\varepsilon_{\text{s}}}{N_{\text{D}}}}$$

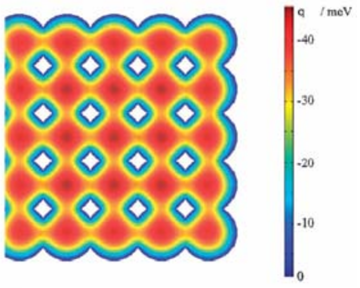
Integration of Gauss's Law for Electricity → Electric Field distribution

Integration of Electric Field → Electrostatic Potential (Φ) distribution

Phys. Chem. Chem. Phys. (2007) 9, 2630-2642 – Peter

DSSC Large Energetic Distribution of States





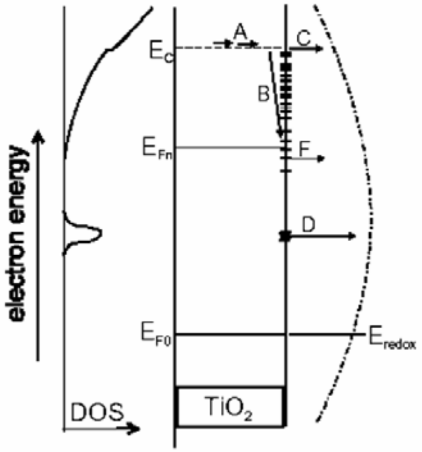
$$W_n \approx 8 L^{n}_{\mathrm{Debye}} = 8\sqrt{\frac{\varepsilon_o \varepsilon_s k_B T}{e^2 N_D}} = C\sqrt{\frac{\varepsilon_s}{N_D}}$$

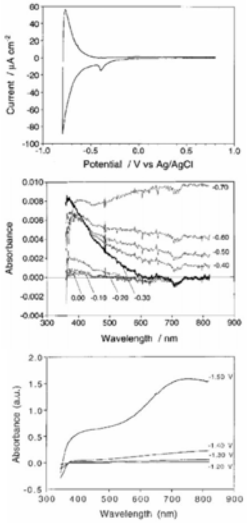
Integration of Gauss's Law for Electricity → Electric Field distribution

Integration of Electric Field → Electrostatic Potential (Φ) distribution

J. Phys. Chem. B (2004) 108, 8016-8022 – Bisquert, Zaban, Hodes, Cahen, Ruhle

Evidence by Spectroelectrochemistry



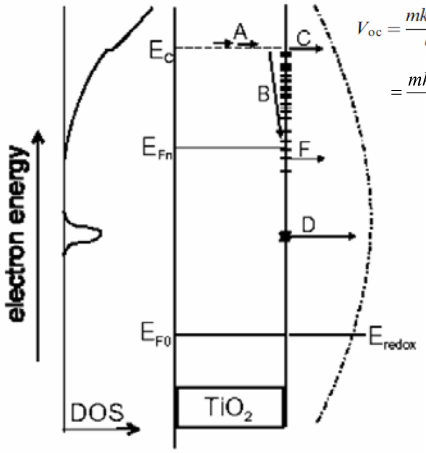


(Show-and-Tell, again: p-type NiO)

Chem. Soc. Rev. (2008) 38, 115-164 – Meyer & Ardo

Voltage

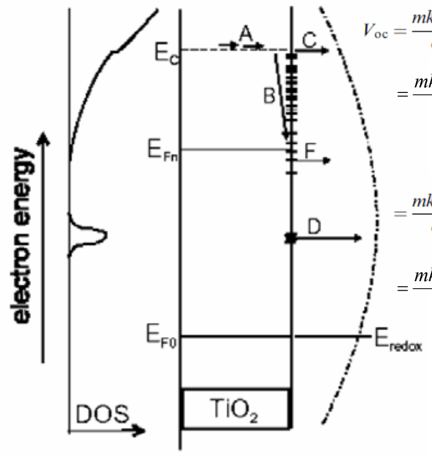
DSSC Density of Acceptor States



$$V_{oc} = \frac{mk_B T}{e}\ln\left(\frac{\mathrm{Rate}^{\mathrm{charge}}_{\mathrm{in}}}{\mathrm{Rate}^{\mathrm{charge}}_{\mathrm{out}}}\right)$$

$$= \frac{mk_B T}{e}\cdot\ln\left(\frac{I}{I_{sat-reverse}}+1\right) \approx \frac{mk_B T}{e}\cdot\ln\left(\frac{I}{I_{sat-reverse}}\right)$$

DSSC Density of Acceptor States



$$V_{\text{oc}} = \frac{mk_{\text{B}}T}{e}\ln\left(\frac{\text{Rate}_{\text{in}}^{\text{charge}}}{\text{Rate}_{\text{out}}^{\text{charge}}}\right)$$

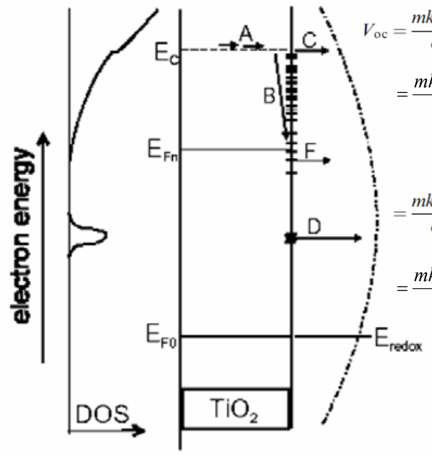
$$= \frac{mk_BT}{e}\cdot\ln\left(\frac{I}{I_{sat-reverse}}+1\right) \approx \frac{mk_BT}{e}\cdot\ln\left(\frac{I}{I_{sat-reverse}}\right)$$

$$= \frac{mk_{\text{B}}T}{e}\cdot\ln\left(\frac{I_{\text{o}}\alpha\phi_{\text{inj}}}{\sum_i k_i[\text{TiO}_2(e^-)]^{\nu_i}\cdot\prod_j [A_{ij}]^{\nu_{ij}}}\right)$$

$$= \frac{mk_BT}{e}\cdot\ln\left(\frac{I_{\text{o}}\alpha\phi_{\text{inj}}}{k_1\left[\text{TiO}_2(e^-)\right]\left[\text{I}_3^{\,-}\right]}\right)$$

Chem. Soc. Rev. (2008) 38, 115-164 – Meyer & Ardo

DSSC Density of Acceptor States



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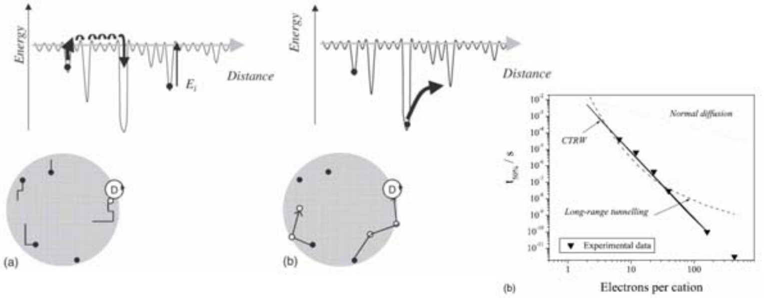
$I^- \rightarrow I^{\cdot} + e^-$
$+ I^- \rightarrow I_2^{\cdot -}$
$+ I_2^{\cdot -} \rightarrow I_3^- + I^-$
$\rightarrow I_2 + I^-$

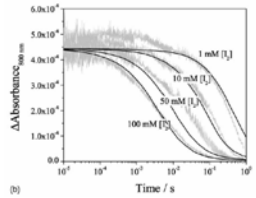
$I_3^- + e^- \rightarrow I_2^{\cdot -} + I^-$
$\rightarrow I^- + I_2 + e^- \rightarrow I_2^{\cdot -} + I^-$
$+ I_2^{\cdot -} \rightarrow I_3^- + I^-$

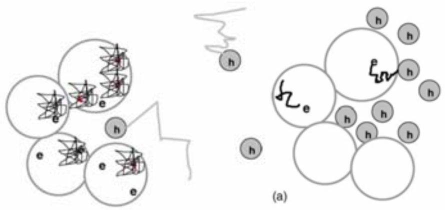
Kinetic Models of Electron Transport

- In fluid solution
  - Second-Order Reaction Mechanism
  - Rate-Limiting, First-Order Reaction Mechanism
- Electron Transport in semiconductors with many traps
  - Interface-Limited, Second-Order Reaction Mechanism
  - Multiple Trapping (time distribution)
  - **CTRW Model (time & location distribution)**
    - **Kohlrausch–Williams–Watts (KWW) stretched-exponential function**
  - Serially Linked Reactions
  - Hopping Model (tunneling between states)
  - MT, Random Flight + Coulomb Trap Model (long hops + attraction)
  - *Second-Order Reaction Mechanism + Transient Electric Field*

MT–CTRW Model from TA Spectroscopy

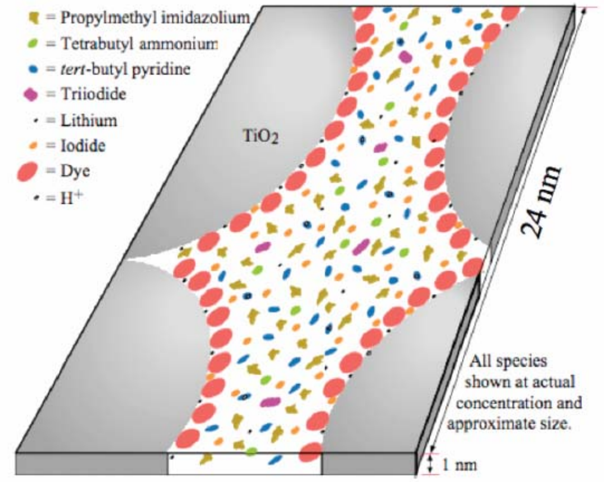




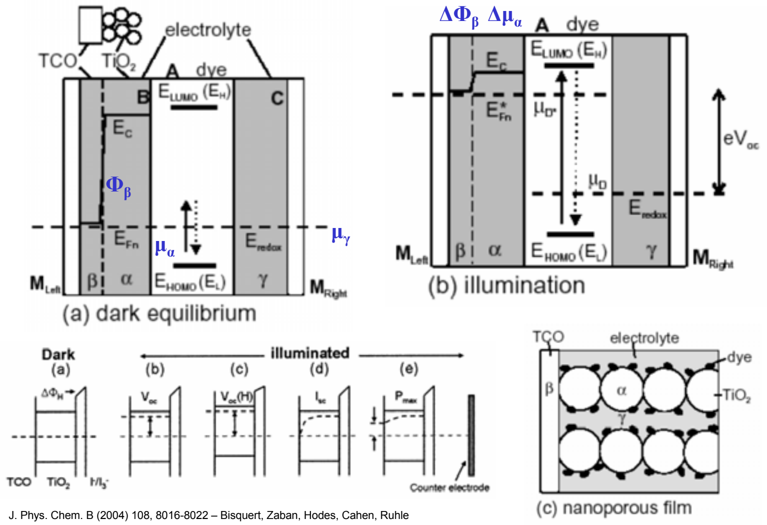


Coord. Chem. Rev. (2004) 248, 1181-1194 – Nelson & Chandler

Ambipolar Diffusion

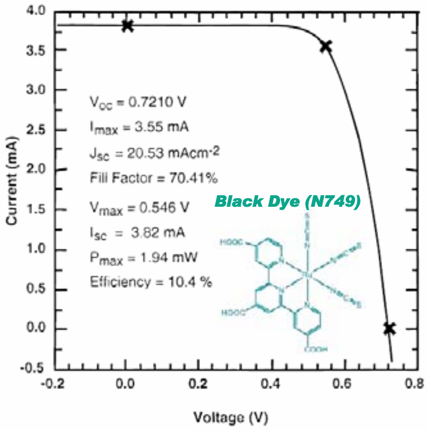


DSSC Method of Action ("No" Field)



J. Phys. Chem. B (2004) 108, 8016-8022 – Bisquert, Zaban, Hodes, Cahen, Ruhle

What is Wrong with a DSSC iV Curve ?



$$\eta = \frac{i_{sc} V_{oc} FF}{P_{sun} A_{cell}} = \frac{j_{sc} V_{oc} FF}{P_{sun}}$$

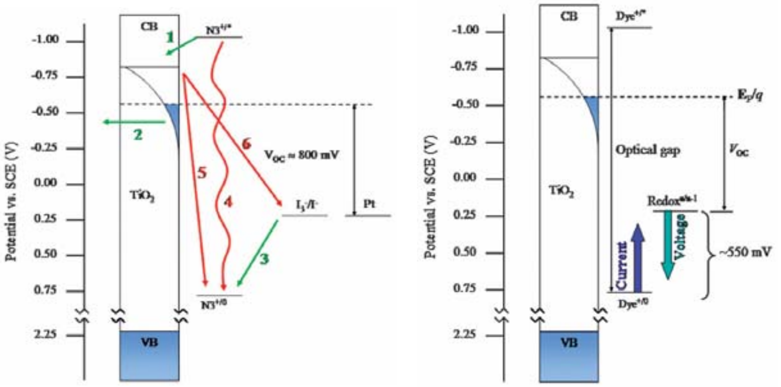
$$FF = \frac{i_{PP} V_{PP}}{i_{sc} V_{oc}}$$

$$\eta_{max(S-Q)} \approx 31\%$$

Why not 100% ?

Acc. Chem. Res. (2000) 33, 269-277 – Gratzel & Hagfeldt

Specifically, Why are DSSCs Imperfect ?



Energy Environ. Sci. (2008) 1, 66-78 – Hupp & Hamann

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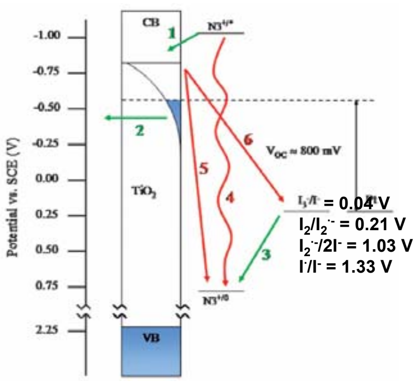
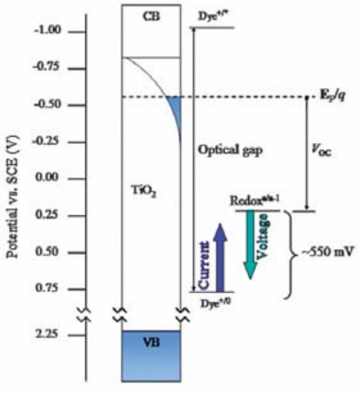


I_3^-/I^- = 0.04 V
$I_2/I_2^{\cdot -}$ = 0.21 V
$I_2^{\cdot -}/2I^-$ = 1.03 V
$I^{\cdot}/I^-$ = 1.33 V

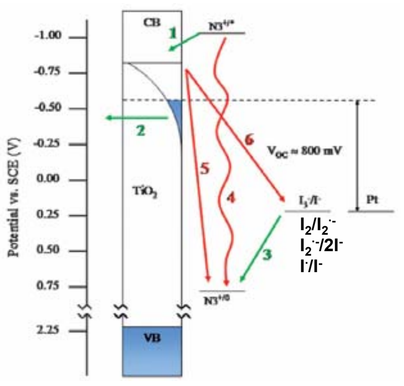


(Draw Iodide Lattimer Diagram on Board)

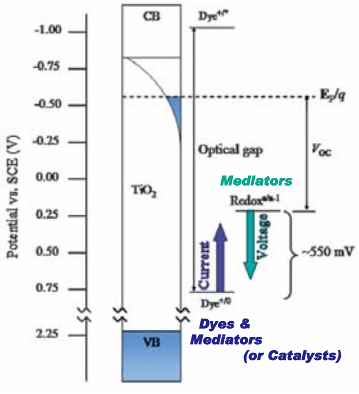
$$\eta = \frac{i_{sc}V_{oc}FF}{P_{sun}A_{cell}} = \frac{j_{sc}V_{oc}FF}{P_{sun}}$$

Chem. Soc. Rev. (2008) 38, 115-164 – Meyer & Ardo

How can we fix them ?



$I_2/I_2^{\cdot -}$
$I_2^{\cdot -}/2I^-$
$I^{\cdot}/I^-$

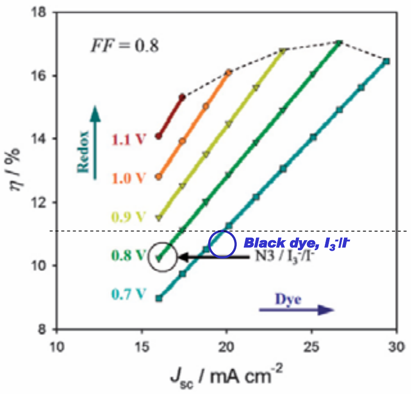


Mediators

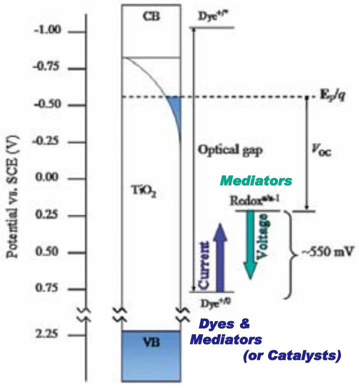
Dyes & Mediators (or Catalysts)

$$\eta = \frac{i_{sc}V_{oc}FF}{P_{sun}A_{cell}} = \frac{j_{sc}V_{oc}FF}{P_{sun}}$$

How can we fix them ?



Black dye, I_3^-/I^-



Mediators

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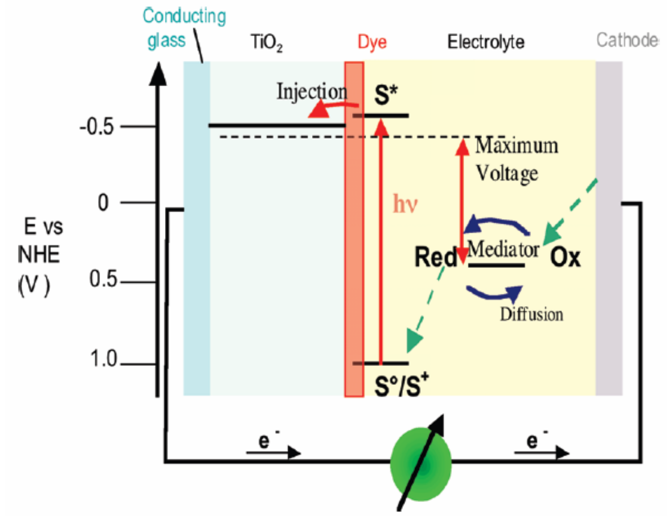
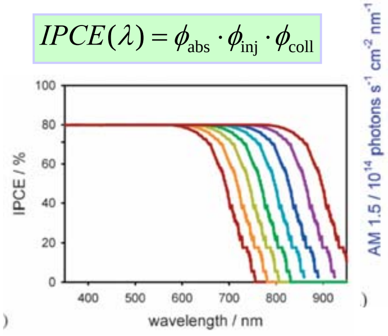
Energy Environ. Sci. (2008) 1, 66-78 – Hupp & Hamann

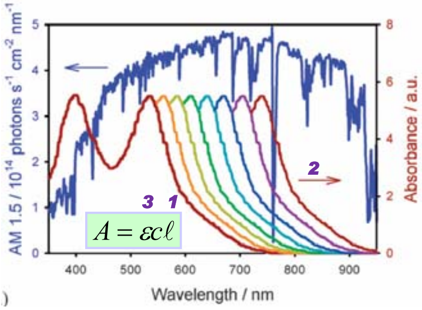
Simplicity of General DSSC Scheme



Engineering Better Light Absorbers

$$IPCE(\lambda) = \phi_{\mathrm{abs}} \cdot \phi_{\mathrm{inj}} \cdot \phi_{\mathrm{coll}}$$





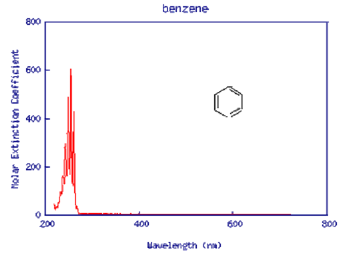
$$A = \varepsilon c \ell$$

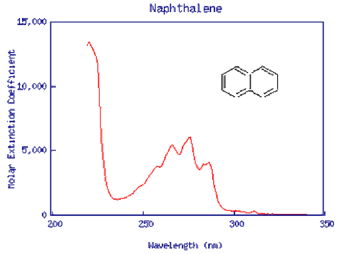
$$j_{\mathrm{sc}} = \int_0^\infty e \cdot IPCE(\lambda) \cdot I_{\mathrm{sun}}(\lambda)\, d\lambda$$

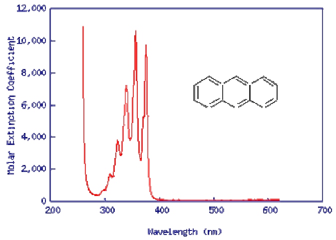
1' $$\ell_{\mathrm{e-:h+}} = \sqrt{D_{\mathrm{e-}} \cdot \tau_{\mathrm{e-:h+}}}$$

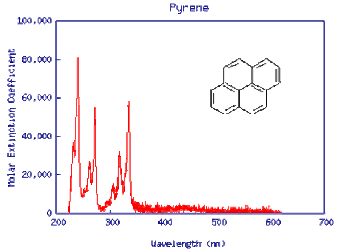
Absorbance (A)	Absorptance (α, %)
0.1	20.6
0.5	68.4
1.0	90
2.0	99
3.0	99.9

2|3) Conjugation = Increased ε and k_r



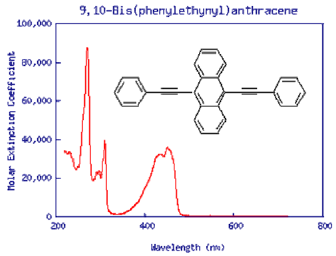


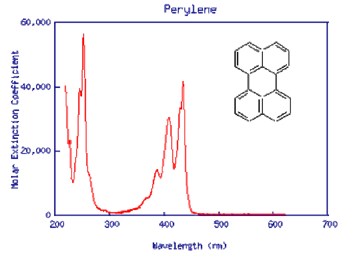


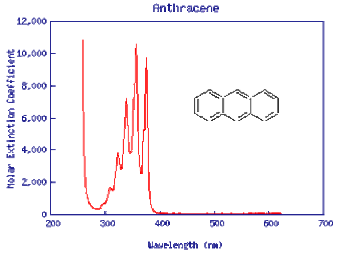


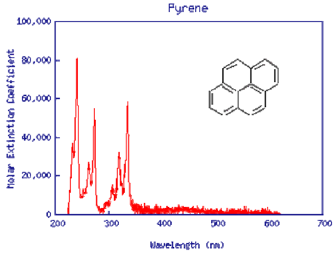
http://omlc.ogi.edu/spectra/PhotochemCAD/html/

2|3) Conjugation = Increased ε and k_r



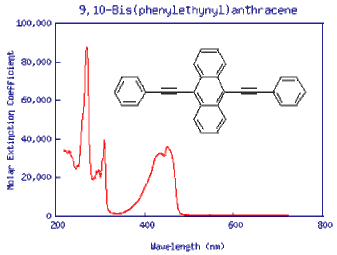


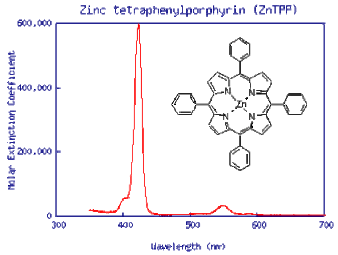


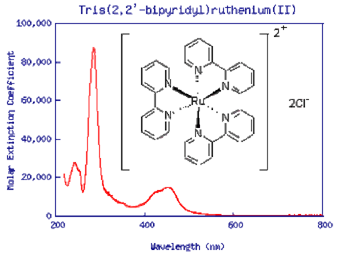


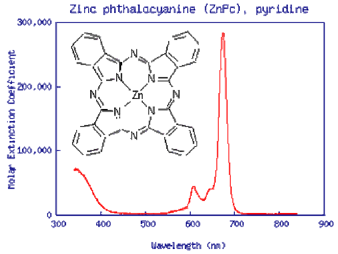
http://omlc.ogi.edu/spectra/PhotochemCAD/html/

2|3) π → π* vs. MLCT vs. π → π*









http://omlc.ogi.edu/spectra/PhotochemCAD/html/

The Confusing Extinction Coefficient

$$IPCE(\lambda) = \phi_{\text{abs}} \cdot \phi_{\text{inj}} \cdot \phi_{\text{coll}} = \alpha(\lambda) \cdot APCE(\lambda)$$

$$\alpha(\lambda) = \phi_{\text{abs}}(\lambda) = \frac{\text{number absorbed}}{\text{number incident photons}} = 1 - \%T = 1 - 10^{-Abs} = 1 - 10^{-\varepsilon c \ell}$$

$$A = \varepsilon c \ell$$

Franck-Condon Principle

$$\text{Prob}_{i \to f} = \frac{2\pi}{\hbar} \cdot \left| \langle \Psi_f | \hat{H}'(t) | \Psi_i \rangle \right|^2 \cdot FCWD$$

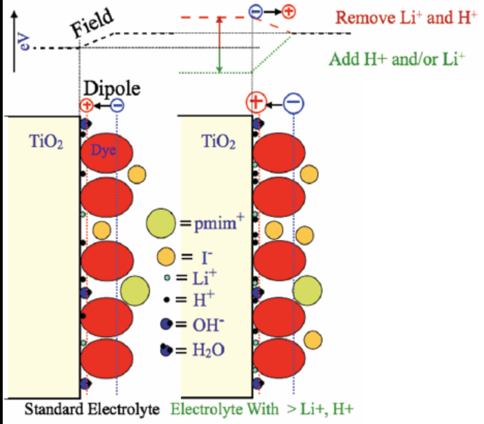
$$\hat{H}'(t) = -\vec{\mu} \cdot \vec{E}(t) = -|\vec{\mu}| |\vec{E}(t)| \cos(\theta)$$

$$\varepsilon(\nu) = \left(\frac{N_A \log(e)}{1000} \right) \left[\frac{2\pi^2 \left| \langle \Psi_f | \hat{H}' | \Psi_i \rangle \right|^2}{3 \varepsilon_o hc} \right] \nu g(\nu - \nu_{ex})$$

MLCT vs. MM(P)CT vs. LM(P)CT vs. LC

(Show-and-Tell, again: Dyed Slides & Make Catechol Film)

Are there ANY Electric Fields ?

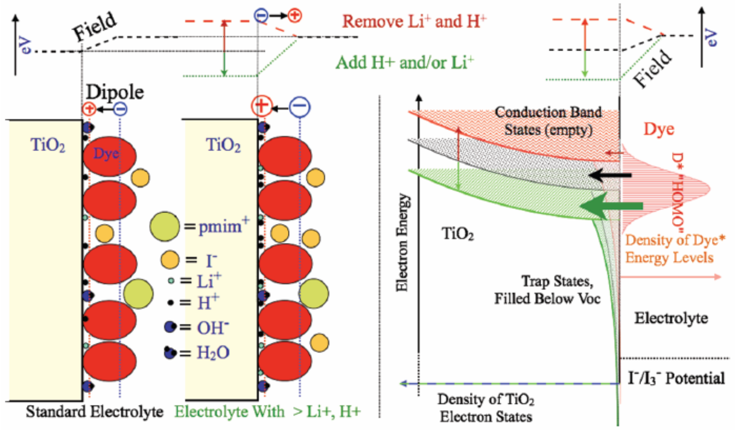


$$L^{\text{n}}_{\text{Debye}} = \sqrt{\frac{\varepsilon_o \varepsilon_s k_B T}{e^2 N_D}} \qquad L_{\text{Debye}} = \sqrt{\frac{\varepsilon_o \varepsilon_s k_B T}{e^2 (c_+ + c_-)}}$$

Gouy–Chapman–Stern Model

Acc. Chem. Res. (ASAP) – Durrant & O'Regan

Are there ANY Electric Fields ?



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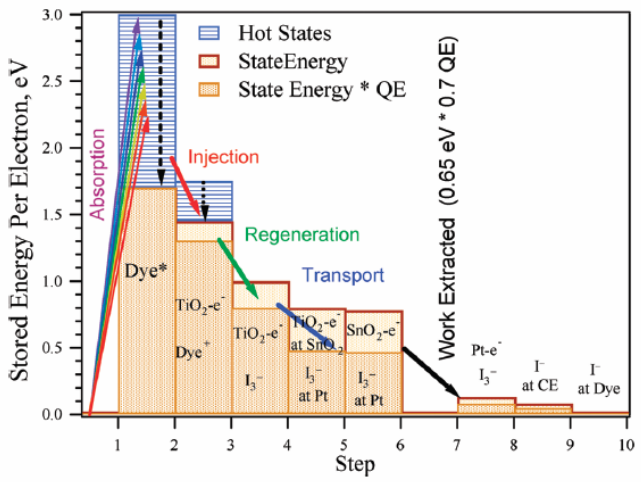
Gouy–Chapman–Stern Model

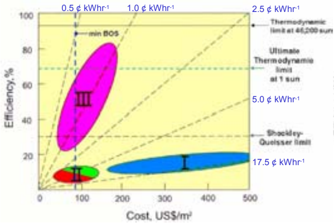
Acc. Chem. Res. (ASAP) – Durrant & O'Regan

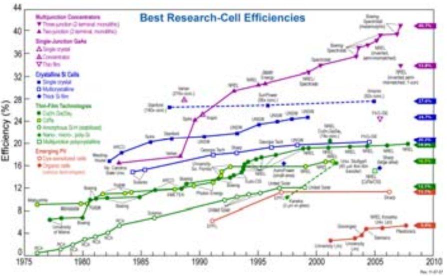
Similar to Nature with Energy Losses



Acc. Chem. Res. (ASAP) – Durrant & O'Regan

Beyond Class I Solar Cells = CHEAPER

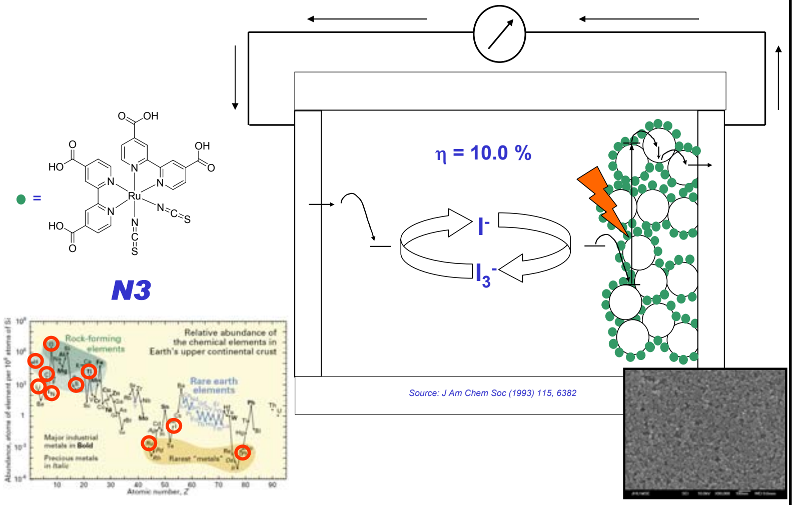




Source: Department of Energy, Basic Research Needs for Solar Energy Utilization (2005)

US DOE, Report of the Basic Energy Sciences Workshop on Solar Energy Utilization. In Basic Research Needs for Solar Energy Utilization, Department of Energy: Washington, DC, 2005 (April 18-21), Figure 2, pg. 14 and Figure 3, pg. 18

Are DSSCs really Class II ?

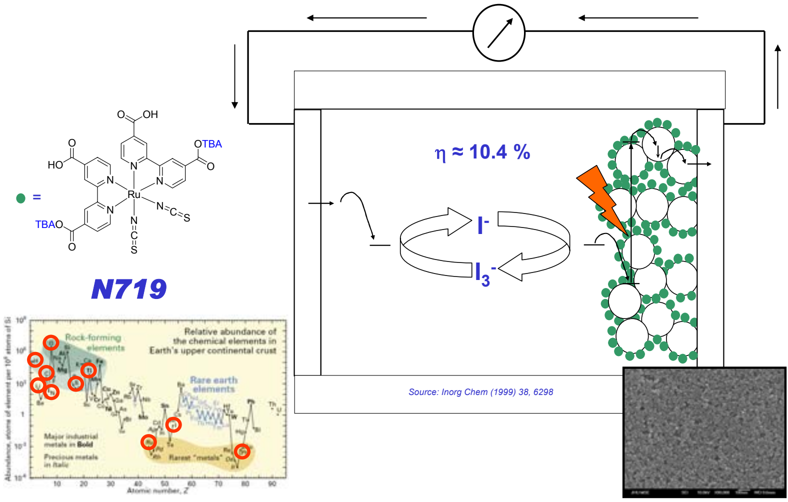


N3

Source: J Am Chem Soc (1993) 115, 6382

US Geological Survey website

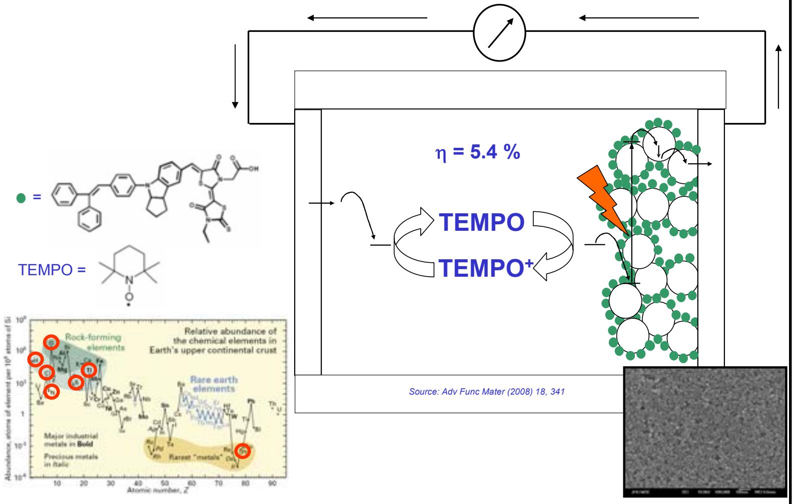
Are DSSCs really Class II ?



N719

Source: Inorg Chem (1999) 38, 6298

With Organic Dyes/Mediators, Maybe



Source: Adv Func Mater (2008) 18, 341

Organic Dyes are doing rather well

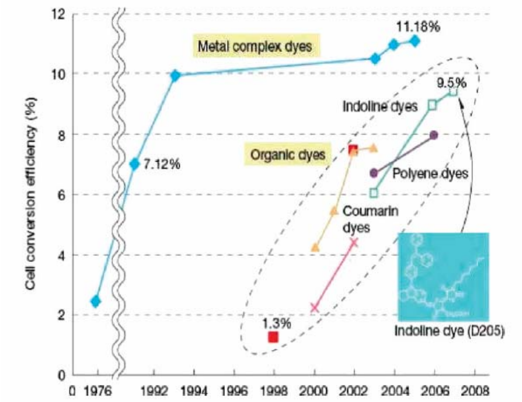
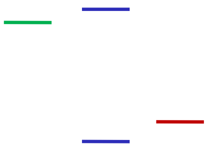


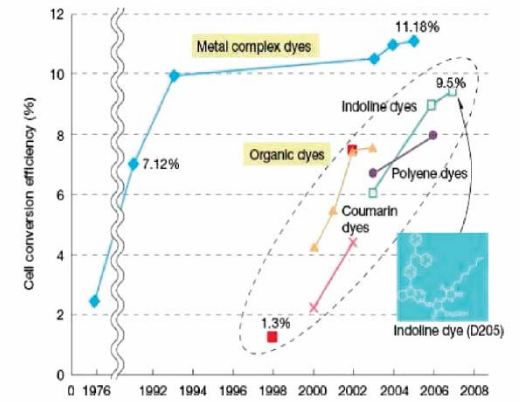
FIGURE 8. Evolution of standard AM 1.5 solar to electric power conversion efficiencies for DSCs based on ruthenium complexes and organic dyes (source: Tetsuo Nozawa *Nikkei Electronics Asia*, July 2008).



A – C – D

Acc. Chem. Res. (ASAP) – Gratzel

Organic Dyes are doing rather well



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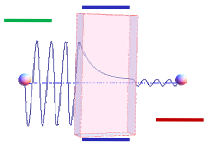
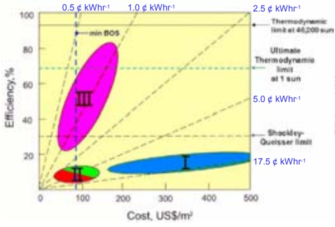
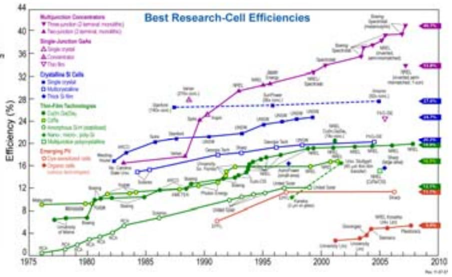


A – C – D

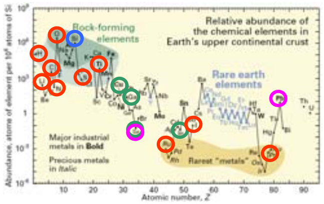
$$k_{ET} = A \cdot \exp\left[-\frac{E_a}{k_B T}\right]$$
$$= A' \cdot \exp[-\beta d] \cdot \exp\left[-\frac{E_a}{k_B T}\right]$$

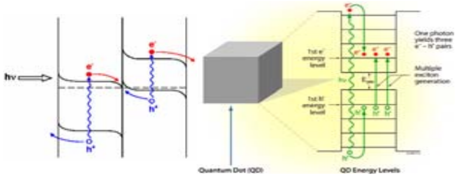
Towards Class III Solar Cells





Source: Department of Energy, Basic Research Needs for Solar Energy Utilization (2005)





US DOE, Report of the Basic Energy Sciences Workshop on Solar Energy Utilization. In Basic Research Needs for Solar Energy Utilization, Department of Energy: Washington, DC, 2005 (April 18-21), Figure 35, pg. 119 and Figure 22, pg. 93

Source: Nature Phys (2005) 1, 189

Cheaper and/or More Efficient DSSCs

- Can one make the TiO_2 film thinner but with a similar LHE?
  - *Increase concentration by making smaller nanoparticles = larger surface area = larger roughness factor*
  - Increase ε: MLCT *vs.* MM(P)CT *vs.* LM(P)CT *vs.* LC
  - Alter the absorption profile
- How can one increase the diffusion length ?
  - Increase D_{e-} $(or\ D_{h+})$
    - Decrease the number of trap states
    - Decrease the number of interparticle necking region connections
  - Increase $\tau_{e-:h+}$
    - Increase the tunneling distance
    - Increase the activation barrier for reverse electron transfer

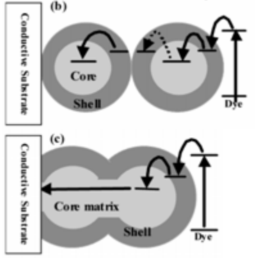
$$\ell_{e-:h+} = \sqrt{D_{e-} \cdot \tau_{e-:h+}}$$

$$A = \varepsilon c \ell$$

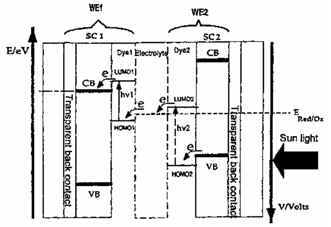
Absorbance (A)	Absorptance (α, %)
0.1	20.6
0.5	68.4
1.0	90
2.0	99
3.0	99.9

GREAT IDEAS !!!

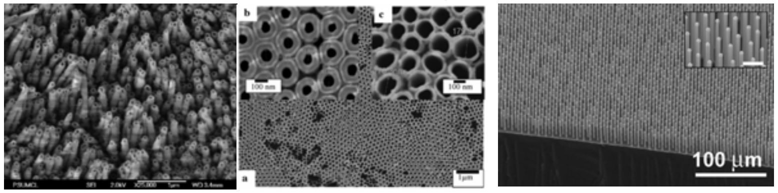
Increase $\tau_{e^-:h^+}$



Increase LHE



Increase D_{e^-}



Langmuir (2002) 18, 3336-3342 – Zaban and J. Phys. Chem. B (2005) 109, 15754-15759 – Grimes and Appl. Phys. Lett. (2007) 91, 103110 – Lewis, Atwater and Patent(1999) – Hagfeldt & Lindquist

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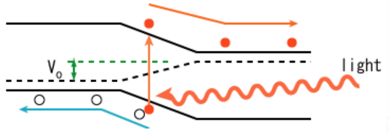
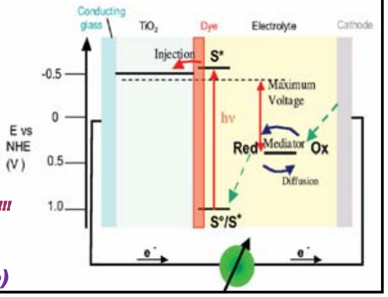
p–n Junction Solar Cells vs. DSSCs

	p–n Junction Cell (~200 μm)	DSSC (~10 μm)
Light absorption	Everywhere; < E_{BG}; Indirect	At dye layer; Spectrum
Initial Charge Separation	Diffusion to + Drift through space-charge region	Immediately at interface
Further Charge Separation	Drift + Diffusion (10 – 40 cm^2/sec)	Diffusion by MT–CTRW and Brownian Motion (10^{-8} – 10^{-4} cm^2/sec)
Charge Recombination	At space-charge region via tunneling	At interface via thermal activation





CIGS ($CuIn_{1-x}Ga_xSe_2$) light absorbers are ~ 3 μm thick !!!

(Draw Schemes on Board to compare)

Conclusions

- Take-home messages
  - Donor – Chromophore – Acceptor Schemes work
    - Activated Unwanted Back Electron Transfer Recombination
    - A Large Tunneling Distance
  - Voltage is limiting ideal Iodide-based DSSCs
    - Increase current with alternative redox mediators and new black(er) sensitizers
    - Fix voltage issues by employing novel redox mediators
  - Light Absorption & Charge Transport are Key (Charge Separation is Ideal)
    - Diffusion length needs to be increased for poorer sensitizers
    - Diffusion length can be decreased by increasing extinction coefficients

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- Hints for HW Question
  - If DSSCs do not have internal space-charge layers, then how do they achieve efficient charge separation ?
  - What is the expected quantum yield for injection if the rate constant for injection is 10^{12} while those for excited-state decay are 10^4 and 10^6 (for radiative (r) and non-radiative (nr) decay), respectively ?