Dye-Sensitized Solar Cells
Basic Principles & Applications

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CIMAV – Chihuahua
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Dye-sensitized TiO₂ solar cells

- photoelectrochemical cell
- porous, high surface area metal oxide film
- light absorption by adsorbed sensitizer molecules
- electron transport in solid and ion transport in solution

Efficiency Record: 11.1%

Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L.Y., Dye-Sensitized Solar Cells with Conversion Efficiency of 11.1%
OUTLINE

• Modules & large-scale applications
• Fundamentals & processes
• Current research topics
• Research at Cinvestav – Mérida
Module:
64 cells of 10 x 10 cm² connected in series

- 10 µm film
- 15 nm TiO₂ particles
- N3 sensitizer
- MPN electrolyte with LiI, DMII, I₂, TBP

Outdoor performance of large scale DSC modules
T. Toyoda et al,
Division of Energy Engineering,
AISIN, SEIKI, Japan
TOYOTA Central R&D Lab.
Japan

Kariya City; N. 35°10' facing South; 30° tilt
Dyesol, Australia

- materials & equipment for fabrication of DSC
- flexible panels for military
- panels on flexible steel with Corus; roofs, etc.

Series interconnect design

IPS 17, Sydney, 2008

10 m² of Dyesol DSC facade panels have been integrated to form a magenta «stripe» across the undulating wall floor-roof of one of the Houses of the Future on display at the Sydney Olympic Park.

2005
Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) at 25°C (IEC 60904-3: 2008, ASTM G-173-03 global).

<table>
<thead>
<tr>
<th>Classification</th>
<th>Effic. (%)</th>
<th>Area (cm²)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</th>
<th>FF (%)</th>
<th>Test centre (and date)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td></td>
<td></td>
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<tr>
<td>Si (crystalline)</td>
<td>25.0 ± 0.5</td>
<td>4.00 (da)</td>
<td>0.706</td>
<td>42.7</td>
<td>82.8</td>
<td>Sandia (3/99)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>UNSW PERL [10]</td>
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<tr>
<td>Si (multicrystalline)</td>
<td>20.4 ± 0.5</td>
<td>1.002 (ap)</td>
<td>0.664</td>
<td>38.0</td>
<td>80.9</td>
<td>NREL (5/04)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>FhG-ISE [11]</td>
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<tr>
<td>Si (thin film transfer)</td>
<td>16.7 ± 0.4</td>
<td>4.017 (ap)</td>
<td>0.645</td>
<td>33.0</td>
<td>78.2</td>
<td>U. Stuttgart (45 μm thick)</td>
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<tr>
<td>Si (thin film submodule)</td>
<td>10.5 ± 0.3</td>
<td>94.0 (ap)</td>
<td>0.492&lt;sup&gt;g&lt;/sup&gt;</td>
<td>29.7&lt;sup&gt;g&lt;/sup&gt;</td>
<td>72.1</td>
<td>FhG-ISE (8/07)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>CSG Solar (1–2 μm on glass; 20 cells) [13]</td>
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<td>III-V Cells</td>
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<tr>
<td>GaAs (crystalline)</td>
<td>26.4 ± 0.8</td>
<td>1.006 (t)</td>
<td>1.030</td>
<td>29.8</td>
<td>86.0</td>
<td>FhG-ISE (3/10)</td>
<td>Fraunhofer ISE</td>
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<td>GaAs (thin film)</td>
<td>26.1 ± 0.8</td>
<td>1.001 (ap)</td>
<td>1.045</td>
<td>29.6</td>
<td>84.6</td>
<td>FhG-ISE (7/08)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Radboud U. Nijmegen [14]</td>
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<td>GaAs (multicrystalline)</td>
<td>18.4 ± 0.5</td>
<td>4.011 (t)</td>
<td>0.994</td>
<td>23.2</td>
<td>79.7</td>
<td>NREL (11/95)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>RTI, Ge substrate [15]</td>
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<td>InP (crystalline)</td>
<td>22.1 ± 0.7</td>
<td>4.02 (t)</td>
<td>0.878</td>
<td>29.5</td>
<td>85.4</td>
<td>NREL (4/90)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Spire, epitaxial [16]</td>
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<td>Thin Film Chalcogenide</td>
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<td>CIGS (cell)</td>
<td>19.4 ± 0.6</td>
<td>0.994 (ap)</td>
<td>0.716</td>
<td>33.7</td>
<td>80.3</td>
<td>NREL (1/08)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>NREL, CIGS on glass [17]</td>
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<td>CIGS (submodule)</td>
<td>16.7 ± 0.4</td>
<td>1.60 (ap)</td>
<td>0.661&lt;sup&gt;g&lt;/sup&gt;</td>
<td>33.6&lt;sup&gt;g&lt;/sup&gt;</td>
<td>75.1</td>
<td>FhG-ISE (3/00)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>U. Upsala, 4 serial cells [18]</td>
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<td>CdTe (cell)</td>
<td>16.7 ± 0.5</td>
<td>1.032 (ap)</td>
<td>0.845</td>
<td>26.1</td>
<td>75.5</td>
<td>NREL (9/01)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>NREL, mesa on glass [19]</td>
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<td>Amorphous/Nanocrystalline Si</td>
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<td>Si (amorphous)</td>
<td>10.1 ± 0.3</td>
<td>1.036 (ap)</td>
<td>0.886</td>
<td>16.75</td>
<td>67.0</td>
<td>NREL (7/09)</td>
<td>Oerlikon Solar Lab, Neuchatel [4]</td>
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<td>Si (nanocrystalline)</td>
<td>10.1 ± 0.2</td>
<td>1.199 (ap)</td>
<td>0.539</td>
<td>24.4</td>
<td>76.6</td>
<td>JOA (12/97)</td>
<td>Kaneka (2 μm on glass) [20]</td>
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<td>Photochemical</td>
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<tr>
<td>Dye sensitized</td>
<td>10.4 ± 0.3</td>
<td>1.004 (ap)</td>
<td>0.729</td>
<td>22.0</td>
<td>65.2</td>
<td>AIST (8/05)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Sharp [21]</td>
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<td>Dye sensitized (submodule)</td>
<td>9.2 ± 0.4&lt;sup&gt;k&lt;/sup&gt;</td>
<td>17.19 (ap)</td>
<td>0.712&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.4&lt;sup&gt;g&lt;/sup&gt;</td>
<td>66.4</td>
<td>AIST (2/10)</td>
<td>Sony, 8 parallel cells [5]</td>
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<td>Organic</td>
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<td>Organic polymer</td>
<td>5.15 ± 0.3</td>
<td>1.021 (ap)</td>
<td>0.876</td>
<td>9.39</td>
<td>62.5</td>
<td>NREL (12/06)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Konarka [22]</td>
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<tr>
<td>Organic (submodule)</td>
<td>3.5 ± 0.3&lt;sup&gt;k&lt;/sup&gt;</td>
<td>208.4 (ap)</td>
<td>8.620</td>
<td>0.847</td>
<td>48.3</td>
<td>NREL (7/09)</td>
<td>Solarmer [23]</td>
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<td>Multijunction Devices</td>
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<tr>
<td>GaInP/GaAs/Ge</td>
<td>32.0 ± 1.5</td>
<td>3.989 (t)</td>
<td>2.622</td>
<td>14.37</td>
<td>85.0</td>
<td>NREL (1/03)</td>
<td>Spectrolab (monolithic)</td>
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<td>GaInP/GaAs</td>
<td>30.3&lt;sup&gt;i&lt;/sup&gt;</td>
<td>4.0 (t)</td>
<td>2.488</td>
<td>14.22</td>
<td>85.6</td>
<td>JQA (4/96)</td>
<td>Japan Energy (monolithic) [24]</td>
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<td>GaAs/CIS (thin film)</td>
<td>25.8 ± 1.3</td>
<td>4.00 (t)</td>
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<td>NREL (11/89)</td>
<td>Kopin/Boeing (4 terminal) [25]</td>
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<td>a-Si/μc-Si (thin submodule)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>11.7 ± 0.4</td>
<td>14.23 (ap)</td>
<td>5.462</td>
<td>2.99</td>
<td>71.3</td>
<td>AIST (9/04)</td>
<td>Kaneka (thin film) [26]</td>
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<td>Organic (2-cell tandem)</td>
<td>6.1 ± 0.2&lt;sup&gt;k&lt;/sup&gt;</td>
<td>1.989</td>
<td>1.589</td>
<td>6.18</td>
<td>61.9</td>
<td>FhG-ISE (7/09)</td>
<td>Heliatek [27]</td>
</tr>
</tbody>
</table>
Advantages DSC:

- inexpensive materials
- inexpensive production process
- low energy content; payback in a few months instead of years
  - performance increases with higher temperature
  - better performance under low light intensity conditions
  - efficiency is less sensitive to the angle of incidence
- flexible cells
- bifacial configuration
- transparency for power windows
- colorful cells
- near-infrared sensitizers: non-colored, transparent PV cells are possible

- outperforms amorphous silicon

Disadvantages

- sealing
- questions on performance stability
- low efficiency compared to silicon and thin films
• absorption of light by the dye, $D^0$, results in a molecule in the excited state, $D^*$
• an electron is injected from $D^*$ into the TiO$_2$ conduction band
• the electron is transported through the nanostructured film to the TCO back contact
• the dye is regenerated by the electron donor in the solution
• the oxidized redox species is, in turn, reduced at the Pt/TCO counter electrode.
Recombination processes

- electron transfer from the TiO$_2$ to:
  - the oxidized dye
  - the electron acceptor in solution
- electron transfer from the TCO to the electron acceptor in solution

Transport processes

- electron transport in the nanostructured, mesoporous film is complicated, and accompanied by ion transport in the solution
- transport is dominated by (ambipolar) diffusion, due to screening effects in the permeating solution
- transport is described by a multiple trapping mechanism, and is non-linear in electron density
New Architectures for Dye-Sensitized Solar Cells
Alex B. F. Martinson, Thomas W. Hamann, Michael J. Pellin, and Joseph T. Hupp

Interface Kinetics

Transport Kinetics

- transport is trap-limited
- transport kinetics become faster at higher $E_F$
- recombination kinetics become faster at higher $E_F$
Current research topics

The nanostructured, mesoporous TiO$_2$ electrode

- large internal surface area: roughness factor 1000
- adequate surface chemistry for dye adsorption
- good internal connectivity for electron transport

C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, and M. Graetzel


Optimization of dye-sensitized solar cells prepared by compression method
G Boschloo, H Lindström, E Magnusson, A Holmberg, A Hagfeldt
*Journal of Photochemistry and Photobiology A: Chemistry* 2002, 148,

Flexible dye-sensitized nanocrystalline semiconductor solar cells
S A Haque, E Palomares, H M Upadhyaya, L Otley, R J Eaton

High-efficiency (7.2%) flexible dye-sensitized solar cells with Ti -metal substrate for nanocrystalline-TiO₂ photoanode

Low-temperature fabrication of dye-sensitized solar cells by transfer of composite porous layers,
New materials, concepts

TiO$_2$ nanotubes
20 µm long
efficiency: 6.9%

Lower temp. processing
Faster electron transport

inverse opal solid TiO$_2$ structure lined with TiO$_2$ nanoparticles:
- thickness: 12 µm
- efficiency: 4%


Successful Dyes - Grätzel group

A: RuL₃
C: RuL₂(SCN)₂(N3)
D: RuL'(SCN)₃

L = 4,4’-dicarboxy-2,2’-bipyridyl-
L’ = 4,4’,4’’-tricarboxy-2,2’:6’,2’’-terpyridyl-

“black dye”

N719

Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO₂-Based Solar Cells
New dyes & electrolyte solutions

Temperature stability: molecular engineering of ruthenium-based dyes

1000 hrs at 80 °C: 94% of initial performance in a quasi-solid state cell.


DSC with eutectic melt of three ionic liquids: 8.2% efficiency maintaining 93% of initial performance after light soaking at 1 sun at 60 °C.

Organic dyes

Ruthenium-based dyes: \(\varepsilon(\text{max}) = 1.4 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}\)

Novel organic dyes: \(\varepsilon(\text{max}) 3 \text{ to } >10 \text{ times higher}\)
allows thinner films!

More viscous electrolyte solutions, ionic liquids, or even
solid-state hole conductors can become more
efficient

stability is still an issue

Indoline dyes
D149: \(\varepsilon(\text{max}) = 6.9 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}\)
D205: \(\varepsilon(\text{max}) = 6.9 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}\)

DSC with low viscosity solvent:
D149: 9.0% efficiency
D205: 7.2% efficiency

Nanoparticle synthesis

• introduction
• nucleation and growth of ZnO nanoparticles from solution
• synthesis of phase-pure TiO$_2$ nanoparticles: anatase, brookite, and rutile

Dye-sensitized solar cells

• efficiency of cells based on TiO$_2$ and ZnO; organic dyes
• numerical calculations of the electrical properties of dye-sensitized solar cells
Controlled Synthesis of Monodisperse Nanoparticles

- control over nucleation and growth processes
- control over aging process

Which experimental parameters affect the nucleation, growth, and phase formation processes?

**Solution-phase synthesis of ZnO nanoparticles:**

\[
\text{ZnCl}_2 + 2 \text{NaOH} \xrightarrow{\text{ethanol, water, RT}} \text{ZnO} + 2 \text{NaCl} + \text{H}_2\text{O}
\]

**Solution-phase synthesis of TiO}_2 \text{ nanoparticles:**}

\[
\text{Ti(IV) iso-propoxide} + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{iso-propanol}
\]
Synthesis kinetics: ZnO nanoparticles

Absorbance is proportional to the total volume of ZnO (for $r << \lambda$):

$$Abs \propto \bar{V} \cdot N$$

with $N =$ particle density

where both the particle density and the average volume per particle are a function of time.

$$1 \text{ mM ZnCl}_2 + 1.6 \text{ mM NaOH} + 50 \text{ mM H}_2\text{O}$$
Effect of Water

1 mM ZnCl$_2$ + 1.6 mM NaOH + x M H$_2$O

- ZnO formation does not occur in the absence of water
- the ZnO formation rate increases with increasing water concentration
- at 200 mM water, nucleation is very fast, and only coarsening is observed
Reaction scheme:

reactants $\rightarrow$ precursor $\rightarrow$ ZnO nuclei $\rightarrow$ growth & coarsening

Precursor Formation:

$\text{ZnCl}_2 + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Zn}_n\text{Cl}_x(\text{OH})_y(\text{H}_2\text{O})_z$

The final structure of the precursor depends on the concentrations of all reactants.

How does the water concentration affect the nucleation kinetics?

- through the solubility of the solid materials:
  at higher water content, the solubility and dissociation of the salts are expected to increase, which would lead to a faster formation of precursor molecules.

- through the precursor structure:
  at higher water content, condensation can occur through olation, which is expected to be faster than oxolation. In the case where $n > 1$, the precursor formation rate would increase with water concentration. If $n = 1$, nucleation could be faster.
**Autohydrolysis**

\[
\text{Zn(OOC-CH}_3\text{)}_2 + H_2O \rightarrow \text{ZnO} + 2 \text{HOOC-CH}_3
\]

**solvent:** iso-propanol (ethanol, etc.)

Particle size distribution can be obtained from the absorbance spectrum:

\[
n(r) \propto -\frac{dA/dr}{4\pi r^3/3}
\]

ZnO nanopowders

Preparation
- 0.1 M ZnCl$_2$ + 0.2 M NaOH in ethanol
- T = 55 °C / 1 hour
- filtered & washed with water to remove NaCl
- dried at 50 °C for 20 hours
- Yield: 4 g for a 500 mL synthesis; practical yield ≈ 90%

Particle size control
- heat at elevated temperature to increase particle size
- increasing water concentration results in increased particle size
Crystalline TiO$_2$ Nanoparticles from Amorphous TiO$_2$

Titanium (IV) isopropoxide in isopropanol

Water/isopropanol stirring at 0 °C

Amorphous titania

Hydrothermal treatment

Anatase

Rutile

Brookite

1.5 M acetic acid; 200 °C

4 M HCl 200 °C

3 M HCl 175 °C

X-ray Diffraction

anatase

rutile

brookite

2θ (°) Intensity (a.u.)
anatase  rutile  brookite

Scherrer equation: the peak width relation between
the grain or
particle size.

<table>
<thead>
<tr>
<th>Material</th>
<th>Radius (nm)</th>
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</thead>
<tbody>
<tr>
<td>rutile</td>
<td>5 nm to &gt;100 nm</td>
</tr>
<tr>
<td>brookite</td>
<td>4 nm to 11 nm</td>
</tr>
<tr>
<td>anatase</td>
<td>3 nm to 15 nm</td>
</tr>
</tbody>
</table>

anatase  rutile  brookite

radius

oskam@mda.cinvestav.mx
Amorphous TiO$_2$

**Amorphous Titania:**
short-range ordering suggests
presence of chains of
octahedral species with Ti - O
- Ti bridges
of 2 - 4 octahedra.

**Anatase:**
highly-crystallized, facetted
nanoparticles of uniform size
After 5 hrs of hydrothermal treatment at 200 °C: presence of nanoparticles, as well as large, compact, rod-shaped agglomerates of nanoparticles which tend to be aligned (oriented attachment of nanoparticles).

After 21 hours (after the change of mechanism observed in the growth kinetics): the nanoparticles recrystallize into large rods.
Brookite

What determines phase formation?

**Total energy considerations:**
- bulk energy: rutile < anatase < brookite
- surface energy: anatase < brookite < rutile

for nanoparticles: anatase has the lowest total energy
lower surface energy results in faster nucleation kinetics

**Precursor chemistry:**
composition and symmetry of precursor molecules determine the crystal structure
(kinetics approach)
Dye-Sensitized Solar Cells

Fabrication:
- synthesis of TiO$_2$ or ZnO nanoparticles from solution
- deposit thin, porous film on FTO-glass
- soak film in dye-solution for 24 hours
- put the platinum-coated TCO-glass on the top, a Surlyn spacer to seal the cell
- add electrolyte solution through holes in the counter electrode
  \[(0.6 \text{ M DMPII} + 0.1 \text{ M LiI} + 0.05 \text{ M I}_2 + 0.5 \text{ M TBP in MPN})\]
- seal the small holes with microscope cover glass and Surlyn.

Anatase-based cell with N-719

ZnO-based cell with N-719

$I_{sc} = 31 \text{ mA}$
$V_{oc} = 2.1 \text{ V}$

15 cm$^2$
65 mW cm$^{-2}$
Dye-sensitized solar cells

(Nanomaterials prepared in our laboratory)

Cells: 0.5 cm²

- TiO₂, η = 6.44%
- ZnO, η = 2.96%

100 mW/cm²

- anatase cells: 6.8%
- brookite cells: 4.0%
- rutile cells: 2%

ZnO cells
(forced hydrolysis): 3.0%

ZnO cells
(electrodeposition): 2.0%
ZnO dye-sensitized solar cells

ZnO cells from Degussa ZnO

<table>
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<tr>
<th>Dye</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>N719</td>
<td>4.4</td>
<td>651</td>
<td>0.60</td>
<td>1.6</td>
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<tr>
<td>Mercurochrome</td>
<td>3.1</td>
<td>667</td>
<td>0.56</td>
<td>0.79</td>
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<tr>
<td>Eosin Y (acid form)</td>
<td>2.5</td>
<td>601</td>
<td>0.52</td>
<td>0.78</td>
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<td>Eosin Y (salt form)</td>
<td>2.7</td>
<td>641</td>
<td>0.60</td>
<td>0.75</td>
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<td>Eosin B</td>
<td>1.0</td>
<td>507</td>
<td>0.43</td>
<td>0.15</td>
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Photovoltaic performance of nanostructured zinc oxide sensitised with xanthene dyes
E Guillén, F Casanueva, J A Anta, A Vega-Poot, G Oskam, R Alcántara, C Fernández-Lorenzo, J Martín-Calleja,

variations in cell stability:

- N719
- Mercurochrome
- Eosin Y (acid form)

2 sun T = 50 °C
Electron Transport in Dye-sensitized TiO₂ Films

- Particles are too small for band bending
- Solution with ions provide shielding
- Electron transport is impeded by transfer to electron acceptor in the solution

steady-state measurements (Lindquist et al.): photocurrent is dominated by diffusion
Band diagram showing trap states in the band gap. The rate constants $k_1$ and $k_{-1}$ denote trapping and de-trapping of electrons, respectively. The Fermi-energy determines which traps dominate the transport kinetics.

### Continuity equation

$$\frac{\partial n}{\partial t} = \frac{1}{e} \frac{\partial J}{\partial x} - R + G$$

### Current density

$$J = en\mu_n \frac{\partial \phi}{\partial x} + eD \frac{\partial n}{\partial x}$$

### Diffusion transport equation

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{n(x,t) - n_0}{\tau_0} + \Gamma \alpha \exp(-\alpha x) = 0$$

The diffusion coefficient and recombination term are dependent to the light intensity. The transport equation is more complex: numerical methods to model electron transport.
Experimental current transients under short circuit conditions

D is a power law function of the light intensity, i.e., the electron density

Electron Transport in Porous Nanocrystalline TiO$_2$ Photoelectrochemical Cells Fei Cao, Gerko Oskam, Gerald J. Meyer, and Peter C. Searson

\[ \frac{\partial n(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( D(n) \frac{\partial n(x, t)}{\partial x} \right) - R + G \]

**GENERATION**

\[ G(x) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \phi_{\text{inj}} I_0 e_{\text{Cell}}(\lambda) \exp \left[ -e_{\text{Cell}}(\lambda) x \right] d\lambda \]

**Injection quantum yield**

\((0 < \phi_{\text{inj}} < 1)\)
\[
\frac{\partial n(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( D(n) \frac{\partial n(x,t)}{\partial x} \right) - R + G
\]

**DIFFUSION**

Electron density-dependent or Fermi level-dependent - diffusion coefficient

\[
D(n) = D_{\text{ref}} f(n) = D_{\text{ref}} \left( \frac{n}{n_{\text{ref}}} \right)^{1-\alpha/\alpha}
\]

\[
g(E) = \frac{\alpha N_t}{kT} \exp \frac{\alpha E}{kT}
\]

\[\alpha = 0.2-0.5\]
Recombination depends the same way on the Fermi-level as diffusion.
Open circuit voltage decay

RECOMBINATION From TCO

CHARGE TRANSFER FROM TCO SUBSTRATE

\[ J_{TCO} = J_{TCO}^0 \left\{ \exp \left[ \frac{-(1-a)eV}{k_B T} \right] - \exp \left[ \frac{aeV}{k_B T} \right] \right\} \]

(Butler-Volmer equation)

\( a \sim 0.5 \)
### EXPERIMENTS & SIMULATION

<table>
<thead>
<tr>
<th>method</th>
<th>measurement</th>
<th>parameter obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UV/vis spectrum</td>
<td>dye absorption coefficient ($\varepsilon_{\text{sol}}(\lambda)$)</td>
</tr>
<tr>
<td>2</td>
<td>steady-state current–voltage curve</td>
<td>dye concentration in cell or quantum yield from $J_{\text{SC}}$ recombination constant at zero bias, $k_R^0$, from $V_{\text{OC}}$ series resistance $R$ from maximum power point</td>
</tr>
<tr>
<td>3</td>
<td>$J_{\text{SC}}$ vs time (current rise upon switching on light)</td>
<td>trap distribution parameter, $\alpha$</td>
</tr>
<tr>
<td>4</td>
<td>$V_{\text{OC}}$ vs light intensity</td>
<td>electron transfer parameter at TCO interface, $b$ + exchange current density at TCO interface, $J_0\text{TCO}$</td>
</tr>
<tr>
<td>5</td>
<td>$V_{\text{OC}}$ vs time (decay upon switching off light)</td>
<td></td>
</tr>
</tbody>
</table>

#### Graphs

- **Graph 1 (J vs t)**: Shows the current density ($J$) over time ($t$) for a TiO$_2$ cell with experimental and modeled data. The models are represented with coloring: experimental (default), Model $\alpha = 0.22$ (red), and Model $\alpha = 0.26$ (green).

- **Graph 2 (V vs t)**: Displays the voltage ($V$) over time ($t$) for a TiO$_2$ cell, with experimental and modeled data using the default and Model colors.
Numerical simulation:
Solving the continuity equation using FTCS + Lax scheme
Experimental Model
Model R=0
ZnO Cell

ZnO/N719/solvent-free electrolyte
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Z Cell (ZnO)</th>
<th>T Cell (TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{Cell}$ ($M$)</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>$k_R^0$ ($s^{-1}$)</td>
<td>9.0 $10^{-7}$</td>
<td>3.1 $10^{-9}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>$b$</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>$J_0$ ($A cm^{-2}$)</td>
<td>1.0 $10^{-4}$</td>
<td>1.1 $10^{-5}$</td>
</tr>
<tr>
<td>$R$ ($\Omega$)</td>
<td>37.5</td>
<td>11.3</td>
</tr>
<tr>
<td>$L$ ($\mu m$)</td>
<td>10.5</td>
<td>180</td>
</tr>
</tbody>
</table>

**Numerical Simulation of the Current-Voltage Curve in Dye-Sensitized Solar Cells** Julio Villanueva, Juan A. Anta, Elena Guillén, and Gerko Oskam

Alternative Recombination Mechanism

\[ \frac{\partial n(x,t)}{\partial t} = \frac{1}{e} \frac{\partial}{\partial x} \left( D(n) \frac{\partial n(x,t)}{\partial x} \right) - R + G \]

**Model 1**

- \[ K = k_0 \left( \frac{\rho}{\rho_0} \right)^{\frac{1-\alpha}{\alpha}} \]
- \[ V_{OC} \propto \frac{kT}{e} \ln(I) \]
- \[ \text{“transport-limited recombination”} \]

**Model 2**

- \[ K = k_0 e^{a \frac{e V}{k_B T}} \]
- \[ V_{OC} \propto \frac{\kappa T}{\alpha + a} \ln(I) \]
- \[ \text{“transfer-limited recombination”} \]
How do materials properties affect the transport & recombination characteristics?

- Through the trap distribution parameters $N_t$ and $\alpha$
- Through the recombination characteristics
  - interactions traps – solution
  - electron transfer properties from the conduction band
  - surface chemistry
Current projects & activities

Synthesis and characterization of metal oxide nanoparticles: TiO$_2$, ZnO, core-shell
- mechanisms of nucleation, growth, and controlled aging

Optimization and application of nanomaterials in the dye-sensitized solar cell
- TiO$_2$ and ZnO nanoparticles
- electrodeposition and electrophoretic deposition of nanostructures

New organic and natural dyes for application in the dye-sensitized solar cell
- extraction, separation, purification, synthesis (Dr. Gonzalo Mena Rejón)
- TD-DFT calculations optoelectronic structure (Dr. Andreas Köster)

Electron transport and recombination mechanisms
- numerical simulations (Dr. Juan A. Anta)
- experimental studies (Professor Laurie Peter; Dr. Petra Cameron)

Hydrogen generation using solar energy
- tandem cells using DSCs and new materials - Fe$_2$O$_3$ and WO$_3$

Nanotoxxicology
- interaction of TiO$_2$ nanoparticles with cell membranes in Tilapia
  (Dr. Omar Zapata, Dr. Romeo de Coss)

Conservation of national monuments – Mayan structures
- nanomaterials for prevention of biofilm formation (Dr. Juan José Alvarado Gil; Dr. Patricia Quintana Owen)
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