Dye Sensitized Solar Cells (DSSCs)
The Solar Spectrum

http://cesp10.phys.utk.edu/ast152/lect/light/spectrum.html
## Table 1.

Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) at 25 °C (IEC 60904-3: 2003, ASTM G-173-03 globall).

<table>
<thead>
<tr>
<th>Classification¹</th>
<th>Effic.² (%)</th>
<th>Area³ (cm²)</th>
<th>Vₘₐₚ (V)</th>
<th>Jₘₐₚ (mA/cm²)</th>
<th>FF ⁴ (%)</th>
<th>Test centre⁵ (and date)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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>42.7¹</td>
<td>82.8</td>
<td>UNSW PERL [18]</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]</td>
<td></td>
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<tr>
<td>Si (thin film transfer)</td>
<td>20.1 ± 0.4</td>
<td>242.6 (ap)</td>
<td>0.682</td>
<td>35.14⁷</td>
<td>77.4</td>
<td>Solarex (43 μm thick) [4]</td>
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<tr>
<td>Si (thin film submodule)</td>
<td>10.5 ± 0.3</td>
<td>94.0 (ap)</td>
<td>0.452²</td>
<td>29.7¹</td>
<td>72.1</td>
<td>CSG Solar (1–2 μm on glass; 20 cells) [20]</td>
<td></td>
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<tr>
<td><strong>III–V Cells</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GaAs (thin film)</td>
<td>28.6 ± 0.9</td>
<td>0.9527 (ap)</td>
<td>1.122</td>
<td>29.68³</td>
<td>86.5</td>
<td>Alta Devices [21]</td>
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<tr>
<td>GaAs (multicrystalline)</td>
<td>18.4 ± 0.5</td>
<td>4.011 (ap)</td>
<td>0.994</td>
<td>23.2</td>
<td>79.7</td>
<td>NREL (11/95)¹</td>
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<tr>
<td>InP (crystalline)</td>
<td>22.1 ± 0.7</td>
<td>4.02 (ap)</td>
<td>0.878</td>
<td>29.5</td>
<td>85.4</td>
<td>Spire, epitaxial [23]</td>
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<td><strong>Thin Film Chalcogenide</strong></td>
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<tr>
<td>CIGS (cell)</td>
<td>19.6 ± 0.6b</td>
<td>0.996 (ap)</td>
<td>0.713</td>
<td>34.8¹</td>
<td>79.2</td>
<td>NREL (4/09)</td>
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<td>CIGS (submodule)</td>
<td>17.4 ± 0.5</td>
<td>15.933 (da)</td>
<td>0.6615¹</td>
<td>33.84¹</td>
<td>75.5</td>
<td>CIGS-ISE (10/11)</td>
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<td>CdTe (cell)</td>
<td>18.3 ± 0.5</td>
<td>1.006 (ap)</td>
<td>0.857</td>
<td>26.95⁵</td>
<td>77.0</td>
<td>NREL (10/12)</td>
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<tr>
<td>CdTe (submodule)</td>
<td>10.1 ± 0.3</td>
<td>1.030 (ap)</td>
<td>0.886</td>
<td>16.75⁷</td>
<td>97.8</td>
<td>Qeriion Solar Lab, Neuchatel [26]</td>
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<tr>
<td><strong>Amorphous/ Nanocrystalline Si</strong></td>
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<tr>
<td>Si (amorphous)</td>
<td>10.1 ± 0.3⁹</td>
<td>1.030 (ap)</td>
<td>0.886</td>
<td>16.75⁷</td>
<td>97.8</td>
<td>NREL (7/09)</td>
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<tr>
<td>Si (nanocrystalline)</td>
<td>10.1 ± 0.2⁹</td>
<td>1.199 (ap)</td>
<td>0.539</td>
<td>24.4</td>
<td>76.6</td>
<td>JQA (12/97)</td>
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<td><strong>Photochemical</strong></td>
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<tr>
<td>Dye sensitised</td>
<td>11.9 ± 0.4⁹</td>
<td>1.005 (da)</td>
<td>0.744</td>
<td>22.47⁹</td>
<td>71.2</td>
<td>AIST (9/12)</td>
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<tr>
<td>Organic</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Organic thin-film</td>
<td>10.7 ± 0.3⁹</td>
<td>1.013 (ap)</td>
<td>0.872</td>
<td>17.75⁹</td>
<td>68.9</td>
<td>AIST (10/12)</td>
<td></td>
</tr>
<tr>
<td><strong>Organic (submodule)</strong></td>
<td>6.8 ± 0.2⁹</td>
<td>395.9 (da)</td>
<td>0.798¹</td>
<td>13.50¹</td>
<td>62.8</td>
<td>AIST (10/12)</td>
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<tr>
<td><strong>Multijunction Devices</strong></td>
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</tr>
<tr>
<td>InGaP/GaAs/InGaAs</td>
<td>37.7 ± 1.2</td>
<td>1.047 (ap)</td>
<td>3.014</td>
<td>14.57⁸</td>
<td>86.0</td>
<td>Sharp [14]</td>
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</tr>
<tr>
<td>a-Si:nc-Si/a-Si (thin film)</td>
<td>13.4 ± 0.4⁹</td>
<td>1.006 (ap)</td>
<td>1.563</td>
<td>9.52²</td>
<td>71.9</td>
<td>NREL (7/12)</td>
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</tr>
<tr>
<td>a-Si:nc-Si (thin film cell)</td>
<td>12.3 ± 0.3³</td>
<td>0.962 (ap)</td>
<td>1.269</td>
<td>12.93¹</td>
<td>69.4</td>
<td>AIST (7/11)</td>
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</tr>
<tr>
<td>a-Si:nc-Si (thin film submodule)</td>
<td>11.7 ± 0.4³</td>
<td>14.23 (ap)</td>
<td>5.462²</td>
<td>2.99</td>
<td>71.3</td>
<td>AIST (9/04)</td>
<td></td>
</tr>
</tbody>
</table>
A different type of “solar system”

Electron-transfer
Between subsystems

External circuit equilibrates
electrical energy
with surroundings

Light energy input
Dye-sensitized solar cells (Grätzel cells)

- Dye-sensitized solar cells (DSSCs) are one of the most promising molecular photovoltaics and have been attracting considerable attention since the pioneering study of Grätzel et al. because of the potential of low-cost production.

- In order to improve the solar-to-electric power conversion efficiency ($\eta$), both metal complexes and metal-free organic dyes, as sensitizers of nanocrystalline TiO$_2$ electrode, have been extensively investigated and developed in terms of optical absorption extension to the red or infrared region through molecular design.

- The highest $\eta$ for DSSCs has so far reached ~15 % obtained from an all solid-state perovskite sensitized TiO$_2$ system.

\[
\eta = \frac{\text{maximum power output (} P_{\text{max}} \text{)}}{\text{power input (} P_{\text{light}} \text{)}}
\]
- A DSSC is comprised of a **photoanode** and **cathode** electrode, with an interstitial **redox mediator** containing electrolyte, connected via an external circuit.

- The photoanode consists of an optically transparent electrode (OTE) surface [typically **fluorine-doped tin oxide** (FTO) glass], with a mesoporous layer (**ca.** 10 mm thickness) of anatase **TiO₂ nanoparticles** (**ca.** 10-20 nm diameter) boasting a remarkable surface area (> 1000 cm⁻²).

- The dye sensitizer is adsorbed on the high surface area TiO₂ by covalent attachment allowing a large absorption cross section (**light harvesting**).

- This adsorption process utilizes appropriate functional groups on the dye molecule for **dye immobilization**, carboxylic and phosphonic acid tethers being the most commonly used.

- The anode (counter electrode) typically consists of platinized FTO glass.
One type of simple photovoltaic device that could be produced in Africa

Schematic of a Graetzel Cell. Red circles are titania aggregates coated with a dye. Pink background is an iodide electrolyte gel. Platinum coated cathode is at the bottom and a clear plastic sheet coated with fluorine doped tin oxide anode is at the top.
Light harvesting in DSSCs
State of the art in DSSCs

CH$_3$NH$_3$PbI$_3$ perovskite sensitized TiO$_2$


Champion molecular based DSSC dyes

\[ I_{SC} = \text{short circuit current (mA)} \]
\[ A = \text{area (cm}^2) \]
\[ J_{SC} = \frac{I_{SC}}{A} = \text{short circuit current density (mA cm}^{-2}) \]
\[ V_{OC} = \text{open circuit voltage (mV)} \]
\[ FF = \text{fill factor} \]
\[ I_0 = \text{incident light flux (mW cm}^{-2}) \]
\[ \eta = \text{power conversion efficiency} \]

**C106 dye**

\[ J_{SC} = 19.78 \text{ mA cm}^{-2} \]
\[ V_{OC} = 758 \text{ mV} \]
\[ FF = 0.779 \]
\[ \eta = 12.10 \% \]

**C219 dye**

\[ J_{SC} = 17.94 \text{ mA cm}^{-2} \]
\[ V_{OC} = 770 \text{ mV} \]
\[ FF = 0.730 \]
\[ \eta = 10.3 \% \]

**YD2-\(\alpha\)-C8 dye**

\[ J_{SC} = 17.30 \text{ mA cm}^{-2} \]
\[ V_{OC} = 965 \text{ mV} \]
\[ FF = 0.71 \]
\[ \eta = 11.9 \% \]
Operation of Dye Sensitized Solar Cells

- Charge separation and charge recombination are competitive!

Semiconductor band energies

- Band positions of several semiconductors in contact with aqueous electrolyte at pH 1.

- The lower edge of the conduction band (red color) and upper edge of the valence band (green color) are presented along with the band gap in electron volts.

- The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference.

- On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential.
Blank TiO$_2$ variable pH study

In each case: Fourth consecutive cycle depicted.

Thickness:
- $x$ and $x$, 4.5µm;
- $x$, 4.4 µm

Voltammogram shifts to positive direction with increased acidity

Conduction band edge shift, in conformity with theory

Compare bare titanium dioxide currents for 5.5m LiTFSI/water solutions of different pH.
Why TiO$_2$?

The cathode material requires several combined properties and...

- Transparent (80%) in the visible
- Ideal electronic band energetics (wide bandgap semiconductor)
- High internal surface area (x700) / porosity (40-60%)
- Chemical and electrochemical stability
- “Right” surface chemistry for modification with dye sensitizers
- Mechanically rugged

...undoped nanocrystalline (10 - 20nm) anatase TiO$_2$ provides these properties.

- Good optoelectronic properties
- Commercially available
- “Proven” nanomaterial
TiO$_2$ films can be printed to achieve reliable device properties.

- Screen-printed film
- 2-12 micron thick
- Uniform coating
- 80+% Transmission in the visible range
- Surface area ca. 85 m$^2$/g
- Good adhesion to substrate
Preparation of TiO$_2$ nanoparticle films

Ti(i-PrO)$_4$ → dil HNO$_3$ → hydrolysis → TiO$_2$ colloid → △ 8 hr. peptidization → TiO$_2$ Sol-gel
→ Autoclave 12 hrs. @ 400 °C → PEG addition → Film Deposition → Sintering 30 min. 450 °C → TiO$_2$ mesoporous film

- TiO$_2$ anatase
- nanoparticles size ~ 20 nm
- thin film thickness ~10 mm

TiO$_2$ anatase Raman

blank & sensitized TiO$_2$ films with ZnTCPP

(a) ZnTCPP
TiO$_2$ & anchoring groups

Scanning electron micrograph of a sintered mesoscopic TiO$_2$ (anatase) film supported on an FTO glass. The average particle size is 20 nm.
The mesoporous nanocrystalline effect

The incident-photon-to-current conversion efficiency (IPCE) is plotted as a function of the excitation wavelength.

- **a)** Single-crystal anatase TiO$_2$.
- **b)** Nanocrystalline TiO$_2$ anatase film.
Incident photon-to-current conversion efficiency

The (IPCE), sometimes referred to also as “external quantum efficiency” (EQE), corresponds to the number of electrons measured as photocurrent in the external circuit divided by the monochromatic photon flux that strikes the cell.

\[
\text{IPCE}_\lambda = \frac{[(hc / e) J_{sc}]}{[I_0 \lambda]}
\]

\[
\text{IPCE}_\lambda = \text{LHE}_\lambda \cdot \phi_{inj} \cdot \eta_{coll}
\]

\(\text{LHE}_\lambda = \text{light harvesting efficiency}\)

\(\phi_{inj} = \text{quantum yield for charge injection}\)

\(\eta_{coll} = \text{charge collection efficiency at FTO electrode}\)

\[
\text{IPCE} = \text{monochromatic efficiency}
\]
DSSC efficiency

\[ \eta = \frac{P_{\text{max}}}{P_{\text{light}}} = \frac{(V_{\text{OC}} \cdot I_{\text{SC}} \cdot ff)}{(I_0 \cdot A) \times 100} = \frac{(V_{\text{OC}} \cdot J_{\text{SC}} \cdot ff)}{I_0 \times 100} \]

By increasing the resistive load on an irradiated cell continuously from zero (short circuit) to a very high value (open circuit) one can determine the maximum-power point, the point that maximizes VxI; i.e., the load for which the cell can deliver maximum electrical power at that level of irradiation.

(The output power is zero in both the short circuit and open circuit extremes)

\( V_{\text{OC}} = \) open circuit voltage

\( I_{\text{SC}} = \) short circuit current

\( A = \) area

\( J_{\text{SC}} = \) short circuit current density = \( I_{\text{SC}} / A \)

\( ff = \) fill factor = \( A_1 / A_2 \)

\( I_0 = \) incident light flux (e.g., AM 1.5)
Kinetic competition in DSCs

- Following absorption of incident light, the dye molecule undergoes rapid transition (< fs) to an excited state electronic configuration.

- This metastable excited state ($\tau_{N719} = 12$ ns) affords rapid charge injection (fs – ps) from the singly occupied, lowest unoccupied molecular orbital (LUMO) into the conduction band (CB) of the TiO$_2$ semiconductor ($E_{CB} = -0.50$ V vs. NHE) thus creating a charge separated state, i.e. TiO$_2$$^\bullet^-$/dye$^\bullet^+$ (charge injection).

- The ensuing fate of this exciton (electron/electron-hole pair) determines the quantum yield for photocurrent generation and thus $\eta$ for the DSC device.

- The excited state electron can diffuse to the back electrode FTO/TiO$_2$ contact (ns – ms) from where it is transported via an external circuit to the counter electrode. In this scenario the ground state dye is regenerated by a redox mediator in the electrolyte (typically $I^-/I_3^-$, $E^0 = 0.35$ V vs. NHE) and the circuit completed by regeneration of the redox mediator at the counter electrode.
(processes in kinetic competition have similar colors)
Nanorod & nanotube electrodes

SEM images of ZnO nanotips films
base diameters ~ 40 nm

Prof. A. Hagfeldt & Dr. G. Boschloo, KTH Stockholm
Prof. Y. Lu, Rutgers Piscataway.

Prof. K. Rajeshwar and Dr. N. de Taccomi
The University of Texas at Arlington

Molecular engineering for DSSCs

- In general, the molecular structure of an organic dye for DSCs has been designed and synthesized based on several basic concepts:

  - **energy matching** of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye with the energy levels of $I^-/I_3^-$ redox potential and $E_{CB}$ of the TiO$_2$ electrode, respectively.

  - a **donor-$\pi$-conjugation-linkage-acceptor (D-$\pi$-A) structure** required for a wide range absorption extending to the near-infrared or infrared region.

  - one or two **anchoring groups** such as carboxylic acid or phosphonic acid groups are required for a strong adsorption onto the surface of TiO$_2$.

  - **Steric/orientational design** strategy for hindering charge recombination processes.
• According to the reports of organic dyes used in DSSCs so far, the combination of a triaryl amine (donor) with a cyanoacrylic acid (acceptor and anchor), brings about good matching of the above-mentioned energy levels.

• Oligothiophenes have been successfully employed as the conjugation unit of the dye molecule between the donor and acceptor groups, resulting in maximum absorption bands shifting to the longer wavelength.

\[ \eta = 10.3\% \]
Effect of Anchor Length on Charge Injection into TiO$_2$

![Chemical structures and absorbance graph]

<table>
<thead>
<tr>
<th>Rod</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>C to N length (Å)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>462 ($1.6 \times 10^4$)</td>
<td>9.6</td>
<td>7.1 (0.35)</td>
<td>56.2 (0.65)</td>
</tr>
<tr>
<td>2</td>
<td>465 ($2.0 \times 10^4$)</td>
<td>16.5</td>
<td>8.7 (0.28)</td>
<td>66.2 (0.72)</td>
</tr>
<tr>
<td>3</td>
<td>465 ($2.0 \times 10^4$)</td>
<td>23.3</td>
<td>12.9 (0.44)</td>
<td>101.4 (0.56)</td>
</tr>
</tbody>
</table>

$^a$ MLCT band, in CH$_3$CN solutions. $^b$ Calculated using Spartan '02 (PM3 minimization). $^c$ Probe at 670 nm.
Effect of Anchor Length on Open Circuit Voltage at TiO₂

\[ V_{oc} = \left( \frac{kT}{e} \right) \ln \left( \frac{I_{inj}}{n \sum k_i[A_i]} \right) \]

- The diode equation predicts a 59 mV increase in Voc for each order of magnitude decrease in the charge recombination rate constant for injected electrons with acceptors, \( k_i[A_i] \), at room temperature provided that the electron injection flux into the semiconductor, \( I_{inj} \), is constant.

- In efficient dye-sensitized solar cells with 1 sun irradiance (100 mW/cm²), the predominant acceptors are thought to be iodide oxidation products, \( I_2 \) and/or \( I_3^- \)

- Charge recombination rates decreased by a factor of 20 for 2 and 280 for 3 relative to 1 when studied in regenerative dye sensitized solar cells.

Iodine/iodide-free redox shuttles for liquid electrolyte-based dye-sensitized solar cells

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• As the most widely used couple, \( I^- / I_3^- \) has a favorable penetration ability into the porous semiconductor film, fast dye regeneration and relatively slow recombination with injected photoelectrons.

• Moreover, \( I^- / I_3^- \) is the only redox couple which has been proven to have long term stability. However, several disadvantages limit its industrial application:
  
  ➢ the corrosion of copper/silver lines, which are used to collect the electrons in large scale modules making the production of long-term stable modules much more difficult
  
  ➢ the \( I_3^- \) and other possible polyiodides formed in the electrolyte absorb a considerable part of the visible light, downgrading the efficiencies of DSSCs.
  
  ➢ The complex redox chemistry in the electrolyte causes great energy loss.
  
  ➢ The redox potential of \( I^- / I_3^- \) limits the photovoltage.

To avoid these disadvantages, new kinds of redox couples have been designed and applied in DSSCs.
\[ V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q} \ln \left( \frac{n}{N_{CB}} \right) - \frac{E_{\text{redox}}}{q} \]

- The Voc can be significantly affected by the redox potential of the electrolyte.
  - \( n \) is the number of photoelectrons in the TiO₂
  - \( N_{CB} \) is the effective density of states of the TiO₂ conduction band
  - \( E_{\text{redox}} \) is the redox potential of the electrolyte redox couple
  - \( q \) is the unit charge.
- Thus, at open-circuit conditions, the number of electrons in the TiO₂, \( n \), is determined by the balance between electron injection and charge recombination.
- From the above eqn it can concluded that the Voc is determined by a selection of processes
  - the irradiation level
  - the properties of the semiconductor conduction band
  - the injection efficiency of the dye
  - the recombination loss rate of photoelectrons
  - the redox potential of the electrolyte redox couple.
\[ V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q} \ln \left( \frac{n}{N_{CB}} \right) - \frac{E_{redox}}{q} \]

- Generally, \( n \) is considerably lower than \( N_{CB} \) and the maximum \( V_{oc} \) is therefore determined by the difference between the \( E_{CB} \) of TiO\(_2\) and the \( E_{redox} \) of the electrolyte.
- Therefore, the redox potential of the redox system plays a key role in the \( V_{oc} \) obtained in a DSSC.
- For the I\(^{-}/I_3^-\) redox couple, the possibilities to increase the \( V_{oc} \) are limited.
- Some modifications can be achieved by changing the concentrations and relative ratio of iodide and iodine, but nevertheless the redox potential of the redox system is more or less fixed.
• Otherwise, in the conventional I⁻/I₃⁻ based electrolyte, the redox mechanisms are complicated. The regeneration is a multi charge-transfer process whose exact mechanism is still debated, but a two-step process is generally accepted.

\[
D^+ + 2I^- \rightarrow D + I_2^- \\
2I_2^- \rightarrow I_3^- + I^- 
\]

• In the first step of the dye-regeneration process, the oxidized dye and iodide lead to the formation of a diiodide radical (I₂⁻).

• The second step follows when the formed I₂⁻ disproportionates into I⁻ and I₃⁻. This leads to a large loss in potential equal to the difference between I⁻ and I₂⁻ redox potentials (approximately 0.4 eV in acetonitrile).
Co(III/II) mediators

- Co^{II}-complexes are commonly in the high spin state, and Co^{III}-complexes are in the low spin state.
- Therefore, Co^{II}-complexes are more reactive than Co^{III}-complexes.
- Co^{II} in the electrolyte performs the function of regenerating the sensitizer in the photoanode because of its higher reactivity.
- At the counter electrode, Co^{III} is catalyzed to obtain an electron, and converted to Co^{II}.
- Co-based complex redox shuttles have the advantage of a tunable redox potential obtained through modification of the ligands.

Fig. 4 The structures of various Co-complexes used in DSCs. The charges of all complexes are either 2+ (reduced form) or 3+ (oxidized form).
Record efficiency for a molecular DSSC sensitizer

Yella et al. Science 2011, 334 (6056), 629-634.
$p$-Type DSSCs (a reverse Graetzel cell)

- Can we take a similar approach to $p$-type DSSCs?
Tandem np-DSSCs

\[ V_{oc} = V_{oc}' + V_{oc}'' \]
Highly efficient photocathodes for dye-sensitized tandem solar cells

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Current-density–voltage characteristics for dyes 1–3; green: 1; blue: 2; red: 3, in a p-type NiO device. c, Current–voltage characteristics of a tandem solar cell (black) as well as p-DSCs (red) and n-DSCs (green) under illumination (AM1.5, 1,000Wm\textsuperscript{-2}, solid lines) and in the dark (dashed lines). Identical NiO and TiO\textsubscript{2} films were used for the construction of the tandem, p- and n-DSC.
Dye-sensitized solar cells

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Abstract

The dye-sensitized solar cells (DSC) provides a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor assume both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Nearly quantitative conversion of incident photon into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM 1.5) to current conversion efficiencies (IPCE) over 10% have been reached. There are good prospects to produce these cells at lower cost than conventional devices. Here we present the current state of the field, discuss new concepts of the dye-sensitized nanocrystalline solar cell (DSC) including heterojunction variants and analyze the perspectives for the future development of the technology.

Keywords: Solar light energy conversion; Dye-sensitized solar cells; Nanocrystalline oxide semiconductor films; Organic hole conductors; Ionic liquids; Ruthenium charge transfer sensitizers

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1. Introduction

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different con-
and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. The phenomenal progress realized recently in the fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell, which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of naocrystalline morphology [1].

2. Operation principle of the dye-sensitized nanocrystalline solar cell (DSC)

A schematic presentation of the operating principles of the DSC is given in Fig. 1. At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO₂ (anatase) although alternative wide band gap oxides such as ZnO [2], and Nb₂O₅ [3] have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. Photo excitation of the latter results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counterelectrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation.

Fig. 2 shows the scanning electron micrograph of a typical TiO₂ (anatase) film deposited by screen printing on a conducting glass sheet that serves as current collector. The film thickness is typically 5–20 μm and the TiO₂ mass about 1–4 mg/cm². Analysis of the layer morphology shows the porosity to be about 50–65%, the average pore size being 15 nm. The prevailing structures of the anatase nanoparticles are square–bipyramidal, pseudocubic and stilblike. According to HRTEM measurements the (1 0 1) face is mostly exposed followed by (1 0 0) and (0 0 1) surface orientations.

A recent alternative embodiment of the DSC concept is the sensitized heterojunction usually with an inorganic wide band gap nanocrystalline semiconductor of n-type polarity as electron acceptor, the charge neutrality on the dye being restored by a hole delivered by the complementary semiconductor, inorganic [4,5] or organic [6] and of p-type polarity. The prior photo-electrochemical variant, being further advanced in development, has an AM 1.5 solar conversion
efficiency of over 10%, while that of the solid-state device is, as yet, significantly lower.

3. Historical background

The history of the sensitization of semiconductors to light of wavelength longer than that corresponding to the bandgap has been presented elsewhere [7,8]. It is an interesting convergence of photography and photo-electrochemistry, both of which rely on photo-induced charge separation at a liquid–solid interface. The silver halides used in photography have band gaps of the order of 2.7–3.2 eV, and are therefore insensitive to much of the visible spectrum, just as is the TiO₂ now used in these photo-electrochemical devices.

The first panchromatic film, able to render the image of a scene realistically into black and white, followed on the work of Vogel in Berlin after 1873 [9], in which he associated dyes with the halide semiconductor grains. The first sensitization of a photo-electrode followed shortly thereafter, using a similar chemistry [10]. However, the clear recognition of the parallelism between the two procedures, a realization that the same dyes in principle can function in both [11] and a verification that their operating mechanism is by injection of electrons from photo-excited dye molecules into the conduction band of the n-type semiconductor substrates [12] date to the 1960s. In subsequent years the idea developed that the dye could function most efficiently if chemisorbed on the surface of the semiconductor [13,14]. The concept emerged to use dispersed particles to provide a sufficient interface [15], then photo-electrodes where employed [16].

Titanium dioxide became the semiconductor of choice. The material has many advantages for sensitized photochemistry and photo-electrochemistry: it is a low cost, widely available, non-toxic and biocompatible material, and as such is even used in health care products as well as domestic applications such as paint pigmentation. The standard dye at the time was tris(2,2'-bipyridyl-4,4'-carboxylate) ruthenium(II), the function of the carboxylate being the attachment by chemisorption of the chromophore to the oxide substrate. Progress thereafter, until the announcement in 1991 [1] of the sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1% under solar illumination, was incremental, a synergy of structure, substrate roughness and morphology, dye photophysics [17] and electrolyte redox chemistry. That evolution has continued progressively since then, with certified efficiency now over 10%.

4. Present DSC research and development

4.1. Panchromatic sensitizers

The ideal sensitizer for a single junction photovoltaic cell converting standard global AM 1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm. In addition, it must also carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface. Upon excitation it should inject electrons into the solid with a quantum yield of unity. The energy level of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimize energetic losses during the electron transfer reaction. Its redox potential should be sufficiently high that it can be regenerated via electron donation from the redox electrolyte or the hole conductor. Finally, it should be stable enough to sustain about 10⁸ turnover cycles corresponding to about 20 years of exposure to natural light.

Much of the research in dye chemistry is devoted to the identification and synthesis of dyes matching these requirements, while retaining stability in the photo-electrochemical environment. The attachment group of the dye ensures that it spontaneously assembles as a molecular layer upon exposing the oxide film to a dye solution. This molecular dispersion ensures a high probability that, once a photon is absorbed, the excited state of the dye molecule will relax by electron injection to the semiconductor conduction band. However, the optical absorption of a single monolayer of dye is weak, a fact which originally was cited as ruling out the possibility of high efficiency sensitized devices, as it was assumed that smooth substrate surfaces would be imperative in order to avoid the recombination loss mechanism associated with rough or polycrystalline structures in solid-state photovoltaics (Fig. 3). This objection was invalidated by recognizing that the injection process produces electron in the

The dilemma of light harvesting by surface immobilized molecular absorbers

A monolayer of dye on a flat surface absorbs at most a few percent of light because its size is much larger than its optical cross section

Compact semiconductor films need to be n-doped to conduct electrons. As a consequence there is energy transfer quenching of the excited sensitizer by the electrons in the semiconductor.

Light harvesting by nanocrystalline TiO₂ films

- Light is absorbed by dye derivatized mesoporous film made of a network of undoped (insulating) TiO₂ nanocrystallites
- The sensitizer is grafted onto the TiO₂ surface through suitable anchoring groups, e.g. carboxylate, phosphonate or hydroxamate.
- Light induced electron injection from the adsorbed dye into the nanocrystallites renders the TiO₂ conductive.

Fig. 3. The dilemma of using flat surfaces for dye-sensitized photovoltaic cells and the advantages of light harvesting by nanocrystalline films.
Fig. 4. Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells.

Fig. 5. Photocurrent action spectra obtained with the N3 (ligand L) and the black dye (ligand L') as sensitizer. The photocurrent response of a bare TiO₂ film is also shown for comparison. Detailed experimental conditions are given in [19].

L = 4, 4′-COOH-2,2′-bipyridine
L = 4,4′,4″-COOH-2,2′:6′,2″-terpyridine

with guanidinium thiocyanate, a self-assembly facilitating additive allowing to increase substantially the open-circuit voltage of the solar cell. These data will be discussed further below.

Fig. 5 compares the spectral response of the photocurrent observed with the two sensitzers. The incident photon to current conversion efficiency (IPCE) of the DSC is plotted as a function of excitation wavelength. Both chromophores show very high IPCE values in the visible range. However, the response of the black dye extends 100 nm further into the IR than that of N3. The photocurrent onset is close to 920 nm, i.e., near the optimal threshold for single junction converters. From there on the IPCE rises gradually until at 700 nm it reaches a plateau of ca. 80%. If one accounts for reflection and absorption losses in the conducting glass the conversion of incident photons to electric currents is practically quantitative over the whole visible domain. From the overlap integral of the curves in Fig. 5 with the AM 1.5 solar emission one predicts the short circuit photocurrents of the N3 and black dye-sensitized cells to be 16 and 20.5 mA/cm², respectively, in agreement with experimental observations. The overall efficiency (η_global) of the photovoltaic cell is calculated from the integral photocurrent density (i_ph), the open-circuit photovoltage (V_oc), the fill factor of the cell (ff) and the intensity of the incident light (I₀ = 1000 W/m²)

\[ \eta_{\text{global}} = \frac{i_{\text{ph}} \times V_{\text{oc}} \times \text{ff}}{I_0} \]

Judicious molecular engineering of the ruthenium dye structure will allow for further increasing the light harvesting in the 700–900 nm region. In this respect ruthenium semiconductor lattice, separated spatially from the positive charge carriers by the dye molecules which are insulating in the ground state and hence provide a barrier for charge recombination. By now, the use of nanocrystalline thin film structures with a roughness factor of over 1000 has become standard practice.

The best photovoltaic performance both in terms of conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitizers having the general structure ML₂(X)₂, where L stands for 2,2′-bipyridyl-4,4′-dicarboxylic acid M is Ru or Os and X presents a halide, cyanide, thiocyanate, acetate, thiocarbamate or water substituent, are particularly promising. Thus, the ruthenium complex cis-RuL₂(NCS)₂, known as N3 dye, shown in Fig. 4, has become the paradigm of heterogeneous charge transfer sensitizer for mesoporous solar cells. The fully protonated N3 has absorption maxima at 518 and 380 nm, the extinction coefficients being 1.3 and 1.33 × 10⁴ M⁻¹ cm⁻¹, respectively. The complex emits at 750 nm the lifetime being 60 ns. The optical transition has metal-to-ligand charge transfer (MLCT) character: excitation of the dye involves transfer of an electron from the metal to the p* orbital of the surface anchoring carboxylated bipyridyl ligand from where it is released within femto- to picoseconds into the conduction band of TiO₂ generating electric charges with unit quantum yield [18].

Discovered in 1993 [19] the photovoltaic performance of N3 has been unmatched for 8 years by virtually hundreds of other complexes that have been synthesized and tested. However in 2001 the “black dye” tri(cyanato)-2,2′/2″-terpyridyl-4,4′/4″-tricarboxylate) Ru(II) achieved a record 10.4% (air mass 1.5) solar to power conversion efficiency in full sunlight [20]. This record has been broken only very recently by using the N3 dye in conjunction
complexes of quaterpyridyl derivatives show great promise [21]. The goal is to obtain a DSC having optical features similar to GaAs. A nearly vertical rise of the photocurrent close to the 920 nm absorption threshold would increase the short circuit photocurrent currently from 20.5 to 28 mA/cm² raising the overall efficiency to about 15%.

An advantage of the DSC with respect to competing technologies is that its performance is remarkably insensitive to temperature change. Thus, raising the temperature from 20 to 60 °C has practically no effect on the power conversion efficiency. In contrast, conventional silicon cells exhibit a significant decline over the same temperature range amounting to ca. 20%. Since the temperature of a solar cell will reach readily 60 °C under full sunlight this feature of the injection cell is particularly attractive for power generation under natural conditions.

4.2. Organic dyes, quantum dot as sensitizers

When considering organic dye structures, porphyrins and phthalocyanines attract particular attention, the former because of the analogy with natural photosynthetic processes, the latter because of their photochemical and phototherapeutic applications. However, porphyrins cannot compete with the N3 or black dye sensitizer due to their lack of red light and near IR absorption. Phthalocyanines do show intense absorption bands in this spectral region. However, problems with aggregation and the unsuitable energetic position of the LUMO level, which is too low for electron transfer to the TiO₂ conduction band have turned out to be intractable so far.

A remarkable advance in the use of organic dyes for DSC was recently made by the group of Hara et al. [22,23]. Using coumarine or polyene type sensitizers, strikingly high solar to electric power conversion efficiencies reaching up to 7.7% in full sunlight have been achieved.

Another strategy to obtain a broad optical absorption extending throughout the visible and near IR region is to use a combination of two dyes which complement each other in their spectral features. Such dye cocktails have already been applied to mesoporous TiO₂ films in the form of mixtures of porphyrines and phthalocyanines. The result was encouraging in as much as the optical effects of the two sensitizers were found to be additive. In particular, there was no negative interference between the co-adsorbed chromophores opening up the way for testing a multitude of other dye combinations [24].

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II–VI and III–V type semiconductors particles whose size is small enough to produce quantum confinement effects. The absorption spectrum of such quantum dots can be adjusted by changing the particle size. Thus, the band gap of materials such as InAs and PbS can be adapted to match the value of 1.35 eV, which is ideal for a single junction solar quantum converter. During the last decade a wealth of information has been gathered on the physical properties of these materials and the research is being pursued very actively. One problem with this approach is the photo-corrosion of the quantum dots which will almost certainly happen if the junction contact is a liquid re-do electrolyte. However they are expected to display higher stability in the solid-state hetero-junction device [25]. The advantage of these sensitizers over conventional dyes is their very high extinction coefficient allowing for use of thinner films of the mesoporous oxide. This should reduce the dark current increasing V₀c and the overall efficiency of the cell.

4.3. Mesoporous oxide film development

When the dye-sensitized nanocrystalline solar cell was first presented perhaps the most puzzling phenomenon was the highly efficient charge transport through the nanocrystalline TiO₂ layer. The mesoporous electrodes are very much different compared to their compact analogs because (i) the inherent conductivity of the film is very low; (ii) the small size of the nanocrystalline particles does not support a built-in electrical field; and (iii) the electrolyte penetrates the porous film all the way to the back-contact making the semiconductor/electrolyte interface essentially three-dimensional. Charge transport in mesoporous systems is under keen debate today and several interpretations based on the Montroll Scher model for random displacement of charge carriers in disordered solids [26] have been advanced. However the “effective” electron diffusion coefficient is expected to depend on a number of factors such as trap filling and space charge compensation by ionic motion in the electrolyte. Therefore the theoretical and experimental effort will continue as there is a need for further in depth analysis of this intriguing charge percolation process. The factors controlling the rate of charge carriers percolation across the nanocrystalline film are presently under intense scrutiny. Intensity modulated impedance spectroscopy has proved to be a an elegant and powerful tool [27,28] to address these and other important questions related to the characteristic time constants for charge carrier transport and reaction dynamics in dye-sensitized nanocrystalline solar cells.

On the material science side, future research will be directed towards synthesizing structures with a higher degree of order than the random fractal-like assembly of nanoparticles shown in Fig. 2. A desirable morphology of the films would have the mesoporous channels or nanorods aligned in parallel to each other and vertically with respect to the TCO glass current collector. This would facilitate pore diffusion, give easier access to the film surface avid grain boundaries and allow the junction to be formed under better control. One approach to fabricate such oxide structures is based on surfactant templates assisted preparation of TiO₂ nanotubes as described in recent paper by Adachi et al. [29]. These and the hybrid nanorod-polymer composite cells developed by Huynh et al. [30] have confirmed the superior photovoltaic performance of such films with regards to random particle networks.
4.4. Higher cell voltage and conversion efficiency through molecular engineering of the interface

The high contact area of the junction nanocrystalline solar cells renders mandatory the grasp and control of interfacial effects for future improvement of cell performance. The nature of the exposed surface planes of the oxide and the mode of interaction with the dye is the first important information to gather. For the adsorption of the N3 dye on TiO₂ this is now well understood. The prevalent orientation of the anatase surface planes is (1 0 1) and the sensitizer is adsorbed through two of the four carboxylate groups, at least one of them being in anchored via a bidentate configuration bridging two adjacent titanium sites [18]. Molecular dynamic calculations employing a classical force field have been carried out to predict the equilibrium geometry of the adsorbed sensitizer state [31,32]. More sophisticated first principle density functional calculations have also been launched recently [33] to model the surface interactions of TiO₂ with simple adsorbates as well as the surface reconstruction effects resulting from the adsorption. The latter approach is particularly promising and will provide an important tool for future theoretical investigations.

Synthetic efforts focus on the molecular engineering of sensitizers that enhance the charge separation at the oxide solution interface. The structural features of the dye should match the requirements for current rectification: in analogy to the photo-field effect in transistors, the gate for unidirectional electron flow from the electrolyte through the junction and into the oxide is opened by the photo-excitation of the sensitizer. The reverse charge flow, i.e. recapture of the electron by the electrolyte could be impaired by judicious design of the sensitizer. The latter should form a tightly packed insulating monolayer blocking the dark current. The gain in open-circuit voltage can be calculated from the diode equation:

\[
V_{oc} = \frac{nRT}{F} \ln \left[ \frac{i_{sc}}{i_o} - 1 \right]
\]  

(2)

where \( n \) is the ideality factor whose value is between 1 and 2 for the DSC and \( i_o \) is the reverse saturation current. Thus for each order of magnitude decrease in the dark current the gain in \( V_{oc} \) would be 59 mV at room temperature. Work in this direction is indispensable to raise the efficiency of the DSC significantly over the 15% limit with the currently employed redox electrolytes.

Important progress to control the self-assembly of the N3 dye at the TiO₂ interface was achieved recently in our laboratory. The strategy employed was to add guanidinium thiocyanate to the electrolyte. The guanidinium cations are adsorbed along with the N3 anions at the interface, screening the lateral coulombic repulsion of the sensitizer and facilitating in this fashion the self-assembly of a compact dye monolayer. This results indeed in a remarkable improvement of the cell voltage due to a reduction in dark current. Using this approach a new record conversion efficiency of 10.6% was achieved recently and Fig. 6 shows current voltage curves obtained with these cells.

4.5. Photovoltaic performance stability

A photovoltaic device must remain serviceable for 20 years without significant loss of performance. The stability of all the constituents of the nanocrystalline injection solar cells, that is, the conducting glass the TiO₂ film, the sensitizer, the electrolyte, the counterelectrode and the sealant has therefore been subjected to close scrutiny. The stability of the TCO glass and the nanocrystalline TiO₂ film being unquestionable investigations have focused on the four other components.

As a pure solid the N3 dye is stable even in air up to 280 °C where decarboxylation sets in. Upon long time illumination it sustained \( 10^8 \) redox cycles without noticeable loss of performance corresponding to 20 years of continuous operation in natural sunlight. The reason for this outstanding stability is the very rapid deactivation of its excited state via charge injection into the TiO₂ occurs in the femtosecond time domain. This is at least eight orders of magnitude faster than any other competing channels of excited state deactivation including those leading to chemical transformation of the dye. The oxidized state of \( \text{N}_3^+ \) the dye produced by the electron injection is much less stable although the \( \text{N}_3/\text{N}_3^+ \) couple shows reversible electrochemical behavior in different organic solvents indicating that the lifetime of \( \text{N}_3^+ \) is at least several seconds under these conditions. However when maintained in the oxidized state the dye degrades through the loss of sulfur. Regeneration of the N3 in the photovoltaic cell should therefore occur rapidly, i.e. within nanosecond or microseconds to avoid this unwanted side reaction. Lack of adequate conditions for regeneration of the dye has led to cell failure [34].

These tests are very important, since—apart from the sensitizer—other components of the device, such as the redox electrolyte or the sealing, may fail under long-term illumination. Indeed, a problem emerged with electrolytes based on cyclic carbonates, such as propylene or ethylene carbonate, which were found to undergo thermally activated decarboxylation in the presence of TiO₂ rendering these solvents unsuitable for practical usage.

These were therefore replaced by a highly polar and nonvolatile solvents, such as methoxypropionitrile (MPN) which do not exhibit this undesirable property. Using a MPN based electrolyte 1 conjunction with a surfactant ruthenium dye, the critical 1000 h stability test at 80 °C was recently passed for the first time with a dye-sensitized solar cell [35].

Room temperature molten salts based on imidazolium iodides have revealed very attractive stability features. Despite their high viscosity impressive overall conversion efficiencies exceeding 6% have been obtained so far [36]. This has been attributed to a Grothus mechanism which increases the diffusion coefficient of the triiodide ions in the melt and to a
very effective mode of charge screening which is operative in this ionic liquids.

Long-term light soaking tests on sealed cells have also progressed significantly over the last few years. These tests are very important, as the redox electrolyte or the sealing, may fail under long-term illumination. A recent stability test 12,000 h of continuous full intensity light exposure has confirmed that this system does not exhibit an inherent instability [37], in contrast to amorphous silicon which due to the Stabler–Wronski effect undergoes photodegradation.

4.6. Solid-state dye-sensitized solar cells

One alternative which offers itself to confront the sealing problem is the replacement of the redox electrolyte by a solid p-type semiconductor interpenetrating the nanocrystalline TiO$_2$ structure which would permit the charge neutralisation of dye molecules after electron injection by its hole transport properties.

Since the sensitizing dye itself does not provide a conducting functionality, but is distributed at an interface in the form of immobilized molecular species, it is evident that for charge transfer each molecule must be in intimate contact with both conducting phases. It is evident that this applies to the porous wide bandgap semiconductor substrate into which the photo-excited chemisorbed molecules inject electrons. It is also evident that in the photo-electrochemical format of the sensitized cell the liquid electrolyte penetrates into the porosity, thereby permitting the intimate contact with the charged dye molecule necessary for charge neutralisation after the electron loss by exchange with the redox system in solution. It is not immediately evident that an interpenetrating network of two conducting solids can so easily be established that an immobilized molecule at their interface can exchange charge carriers with both. However results are promising. The charge transport materials are deposited by spin coating from the liquid phase in order to achieve the necessary intimate contact, thereby introducing a solution of the conducting compound into the previously sensitized
nanostructure. The charge transfer material currently used is a spirobifluorene:

Since the first report on this system in 1998 its photovoltaic conversion efficiency has been improved considerably and stands presently at 3.2% [38]. An even higher efficiency of 3.8% was recently achieved by Meng et al. using a dye-sensitized solar cell containing Cu(I) as a hole conductor instead of a liquid electrolyte [39].

5. Conclusions

The dye-sensitized nanocrystalline electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity. It is the prototype of a series of optoelectronic and energy technology devices exploiting the specific characteristics of this innovative structure for oxide and ceramic semiconductor films. Recent developments in the area of sensitizers for these devices have lead to dyes which absorb across the visible spectrum leading to higher efficiencies. The recent development of an all solid-state heterojunction dye solar cell holds additional potential for further cost reduction and simplification of the manufacturing of dye solar cells.

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