Dye-sensitized Solar Cells (DSCs) Based on Nanocrystalline TiO$_2$ and Recent Progress in Taiwan

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ENERGY OPTIONS

Non-renewable
- Fossil fuels
  - Coal
  - Oil
  - Natural gas
- Nuclear fuels
  - Radioactive materials
- Dye-sensitized Solar Cells (DSCs)

Renewable
- Wind
- Hydro
- Solar
- Biomass
- Ocean
- Geothermal
OUTLINE

- Background
- Photocathode or Counter Electrode
- Electrolyte
- Dye
- TiO₂ Photoanode
- Concluding Remarks

BACKGROUND

- DSC: the 3rd generation of solar cells
- The Inspiration

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{Chlorophyll} + \text{Sunlight} = \text{Oxygen} + \text{Carbohydrates}
\]

DSCs

Electrolyte + Dye + Sunlight = Energy
Basic Structure and Reaction Paths

$3I^3(A) + 2e^- (\text{counter electrode}) \rightarrow 3I^-(A^-)$

dye (S) + $hv \rightarrow$ dye$^*(S^*)$

dye (S) + TiO$_2$ $\rightarrow$ e$^-$(TiO$_2$) + oxidized dye (S$^*$)

oxidized dye (S$^*$) + $I^-(A^-) \rightarrow$ dye (S) + $I^3(A)$

"Dye sensitized solar cell"

Population: Taiwan/World = ~0.33%
PHOTOCATHODE OR COUNTER ELECTRODE

- Mostly Pt-coated
  - Thermal evaporation
  - Sputter deposition
  - Thermal decomposition of chloroplatinic acid followed by heat treatment (450 °C)
- Activity of Pt is important for the reduction of the tri-iodide ions.

Counter Electrodes Having CNTs

- The DSC containing the PEDOT films with 0.6 wt.% of MWCNT on stainless steel as counter electrode had the best cell performance of 8.08%
ELECTROLYTE

- Liquid Electrolyte
  - Tri-iodide/Iodine redox system
  - Redox potential ~ 0.4 vs NHE
- Gel Electrolyte
- Solid-state Electrolyte

Gel Electrolyte

The characteristics of liquid electrolyte
- reduced the dye fast (high ionic conductivity)
- penetrate into the TiO₂ easily

Problems of liquid electrolyte in solar cell
- difficulty in long-term sealing (leakage of electrolyte)
- volatility of electrolyte
- toxicity of electrolyte
- desorption of dye

Prepare gel state electrolyte for solar cell
Polyvinyl Acetate (PVA) and Polyacrylonitrile (PAN) have different glass transition temperatures (Tg).

<table>
<thead>
<tr>
<th>System</th>
<th>η (%)</th>
<th>F.F.</th>
<th>Isc</th>
<th>Voc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid (MPN-based)</td>
<td>6.57%</td>
<td>0.63</td>
<td>14.3</td>
<td>735.3</td>
</tr>
<tr>
<td>Sol state</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA -15w%</td>
<td>5.02%</td>
<td>0.59</td>
<td>12.14</td>
<td>689.8</td>
</tr>
<tr>
<td>PVA -30w%</td>
<td>4.98%</td>
<td>0.61</td>
<td>11.6</td>
<td>705.4</td>
</tr>
<tr>
<td>Insolubility</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poly (AN-co-VA), copolymer (3w%)</td>
<td>5.51%</td>
<td>0.61</td>
<td>12.2</td>
<td>738.5</td>
</tr>
</tbody>
</table>

**Polyvinyl Acetate (PVA)** and **Polyacrylonitrile (PAN)** are used in different systems for photovoltaic applications.

The diagram shows the relationship between potential and photocurrent density for different systems, indicating higher efficiency and conversion under certain conditions.
**Categories of Dyes**

- Ru-complex sensitizer
  - N3, N719

- Organic sensitizer
  - D-π-A systems: D149, D205, YD-2

**Engineering of Dye Molecules**

- N749 Ru(SCN)$_3$L’
  - (L’=4,4’,4”-tri carboxy-2,2’:6’,2”-terpyridine)
Thiophene: C₄H₄S

N3: 7.7%  
CYC-B1: 8.54%  
CYC-B11: 11.5%

\[
\begin{align*}
\text{Absorbance (a.u.)} & \quad \text{Wavelength (nm)} \\
0.1 & \quad 300 \quad 400 \quad 500 \quad 600 \quad 700 \quad 800 \\
\end{align*}
\]

\[
\begin{align*}
\text{Molar Absorbance (L mol}^{-1} \text{cm}^{-1}) & \quad U / V \\
0 & \quad 0.4 \quad 0.6 \quad 0.8 \\
\end{align*}
\]

The higher value of $\eta$ of the CBTR-sensitized cell (relative to that of the N719 cell) arose from its higher value of Jsc, which attributed to the presence of the NHC ligand (a strong $\sigma$ donor).
Dye: Thiocyanate (NCS) free

TFRS-2: 1000h illumination at 60°C efficiency from 6.65 to 6.32%

Organic Sensitizer Dye

Organic dyes with large conversion efficiencies are typically composed of a donor-π-acceptor (D–π–A) structure with a well defined architecture.

$e^-$

D  π  A  TiO$_2$
**Porphyrin-based**

2.4 μm thick
YD-2/D-205: 6.9% (world record)
YD-2: 5.6%

An 11% (11 μm + 5 μm) solar-to-electric power conversion efficiency by using YD-2 dye
(World Record Organic dye)

**TiO₂ PHOTOANODE**

RDSC
Hydrothermally Synthesized TiO₂ Nanopowders

Highly Effective TiO₂ Blocking Layer

Effects of Sintering & Surface Treatment Conditions

FDSC
Two-step Synthesized TiO₂ Mesoporous Beads
- Excellent Optical Scattering Effects
- Ultra-fast Electron Transport Rates

Binder-free Process
Electron Transport/Transfer

1. Electron injection
2. Charge collection
3. Regeneration
4. Luminescence
5. Recombination
6. Interception

Hydrothermal Synthesis of TiO₂ Nanopowders

<table>
<thead>
<tr>
<th>No.</th>
<th>Conc.</th>
<th>T</th>
<th>Citric acid</th>
<th>Time</th>
<th>TiO₂ phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.9M</td>
<td>0°C</td>
<td>Pre-added</td>
<td>4hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>2.</td>
<td>0.9M</td>
<td>0°C</td>
<td>Post-added</td>
<td>4hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>3.</td>
<td>0.9M</td>
<td>0°C</td>
<td>None</td>
<td>4hr</td>
<td>Rutile</td>
</tr>
<tr>
<td>4.</td>
<td>0.9M</td>
<td>RT</td>
<td>Post-added</td>
<td>4hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>5.</td>
<td>0.1M</td>
<td>0°C</td>
<td>Post-added</td>
<td>2hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>6.</td>
<td>1.5M</td>
<td>0°C</td>
<td>Post-added</td>
<td>2hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>7.</td>
<td>0.9M</td>
<td>0°C</td>
<td>Post-added</td>
<td>2hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>8.</td>
<td>0.9M</td>
<td>0°C</td>
<td>Post-added</td>
<td>10hr</td>
<td>Anatase</td>
</tr>
<tr>
<td>9.</td>
<td>P25</td>
<td></td>
<td></td>
<td></td>
<td>Rutile+Anatase</td>
</tr>
</tbody>
</table>
Oxygen vacancy concentration dominated effect
The increase in the cell efficiency is attributed to the interplay among:
- reduced oxygen vacancies
- a higher C-C sp² to sp³ bonding ratio
- a better incident photon to conversion efficiency
- enhanced dye

Highly Effective TiO₂ Blocking Layers (FDSC)

- Sputter-deposited, 10-nm TiO₂ as blocking layer
  - Reports show that
  - the required thickness ranges from 100 to 200 nm
  - the exclusively used crystalline phase of a TiO₂ blocking layer is anatase.
Effective blocking to reduce the dark current
TiO$_2$ Mesoporous Beads for FDSC

1. Excellent Optical Scattering Effects
2. Having Ultra-fast Electron Transport Rates

A TiO$_2$ bead is a spherical particle consisting of many TiO$_2$ nanoparticles.

Sol-gel process + Hydrothermal process

Sample B 5 μm P25  Samples C to F  5 μm Beads
3 μm P25  3 μm P25

Percentage Increase

$J_{sc}$  $V_{oc}$  FF  $\eta$
**Bind-free Process for FDSC**

- **TiO$_2$ suspension solution**: P25 powder + ethanol + acetylacetone
- **Charge solution**: iodine + ketone + DI water

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**CONCLUDING REMARKS**

- Dyes have been modified for improving absorption and the efficiency. Ruthenium complex (CYC-B11) 11.5% and Porphyrin based (YD-2) 11% dyes have given the best efficiency as compared to N3/N719.
- Using 0.6% MWNT in PEDOT-PSS as counter electrode produced an efficiency of 8.08% on SS substrate, 7.71% on FTO as compared to 7.7% for conventional Pt on FTO.
- PAN-VA based gel electrolyte produced an efficiency 6.43% and very close to the conventional liquid electrolyte (6.57%) under similar conditions.
- **Anode**:
  - Binder free paste by electrophoresis produced an efficiency as high as 4.57% for flexible PEN substrates.
  - TiO$_2$ blocking layer improved the efficiency by 25% in flexible PEN substrate.
  - Graphene modified TiO$_2$ paste improved the efficiency of cell by 28%.
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Thank you for your attention