Nanowire Solar Cells

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Emerging PV

- Low cost
- Intermediate efficiency
- Environmental benign
- Possible solar paint
Emerging PV

Why nanowires are important?

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PV Performance Metrics

\[ FF = \frac{J_M V_M}{J_{SC} V_{OC}} \]

\[ Efficiency = \frac{P_{out}}{P_{in}} = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \]
\[ \eta_A = (1 - e^{-\alpha d}) \]

\[ \eta_{ED} = e^{-d/L_D} \]

\[ \text{IQE}(\lambda) = \eta_A(\lambda) \eta_{ED} \eta_{CT} \eta_{CC} \]

\[ \eta_{PCE} = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{FF \times V_{OC}}{P_{\text{in}}} \int q F(\lambda)\text{IQE}(\lambda)d\lambda \]
Emerging PV

- Use of solar at terawatt levels requires drop in $/W_p$

- **3N:** New materials, New designs, New tricks
  
  - "dirty" semiconductors
    - organics
    - oxides
    - absorbers
    - biological subunits
  
  - dye-sensitized cells
  
  - bulk heterojunction cells
    - (polymer, organic-inorganic)
  
  - quantum effects
    - carrier multiplication
    - frequency shifting
    - Interface engineering

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Dye-sensitized Photoelectrochemical Cell


DSC characteristics
- surface area of 800 – 1000 cm² per cm²
- η of 5 -10% with TiO₂ nanoparticles
- electron transport via trap-mediated diffusion
- Low efficiency at long wavelength

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The three ways to improve DSC efficiency

1) Find dyes that function efficiently across the visible and near-IR
2) Raise open-circuit voltage closer to its theoretical maximum
3) Increase the electron diffusion length in the oxide anode, \( L_d = (D_e \tau)^{1/2} \)

- speed up electron transport
- slow recombination
- adopt a nanowire geometry
- engineer the active interface

<table>
<thead>
<tr>
<th>Nanoparticle DSC</th>
<th>Nanowire DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>random, polycrystalline network</td>
<td>oriented single-crystalline channels</td>
</tr>
<tr>
<td>slow diffusive transport</td>
<td>fast band conduction (field-assisted)</td>
</tr>
<tr>
<td>efficient for films ( \sim 10 ) ( \mu )m thick</td>
<td>in principle, efficient for much thicker cells</td>
</tr>
</tbody>
</table>

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\( D_e \) is electron diffusion coefficient, \( \tau \) is the lifetime of the excitons.
## Nanowire DSC: Design Principle

- **high nanowire density**
- **long, thin nanowires**

<table>
<thead>
<tr>
<th>electrode</th>
<th>length (µm)</th>
<th>diameter (nm)</th>
<th>density (x10^10 cm^-2)</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoparticle</td>
<td>8 - 10</td>
<td>15 - 30</td>
<td>n/a</td>
<td>800 - 1000</td>
</tr>
<tr>
<td>ideal nanowire</td>
<td>20</td>
<td>60</td>
<td>3</td>
<td>1080</td>
</tr>
<tr>
<td>achieved NW</td>
<td>20</td>
<td>130</td>
<td>0.3</td>
<td>~200</td>
</tr>
</tbody>
</table>

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Large-Scale Nanowire Array Synthesis

1\textsuperscript{st}: dip-coat to get ZnO quantum dots

2\textsuperscript{nd}: grow nanowires from QD seeds

- Nanowire densities of 1-40 billion cm\(^{-2}\)
- Single-crystalline wires in direct contact with the substrate
- Inexpensive and environmentally benign
- Compatible with arbitrary substrates of any size

Poly-ethylenimine (PEI):

$$H_2N-(CH_2CH_2N)_x-(CH_2CH_2NH)_y-\text{CH}_2\text{CH}_2\text{NH}_2$$

Control of Nanowire Aspect Ratio

<table>
<thead>
<tr>
<th>DSC</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspect ratio &gt; 150</td>
<td>aspect ratio = 10</td>
</tr>
</tbody>
</table>

**Graph:**
- Diameter (nm) vs. Length (microns)
- Black squares: without PEI
- Red circles: with PEI

**Images:**
- Hybrid: aspect ratio = 10
- DSC: aspect ratio > 150

**Scale:**
- 500 nm
- 5 μm
Alignment Control

High Optical Quality

- TEM shows that the nanowires are single crystals
- Wire surfaces are clean (Raman, EELS) after 400 °C treatment
**Characterization of Nanowire Arrays**

**Electrical:** Ohmic wire-substrate contacts

- Individual wires are electrically conductive
  \[ \rho = 0.1 - 1 \ \Omega \ \text{cm} \]
  mobility: 1-5 cm²V⁻¹s⁻¹
  electron diffusivity: \( D_n = 0.05-0.5 \ \text{cm}^2\text{s}^{-1} \) \([D = k_B T \mu / e]\)

Ensure larger electron diffusion length, avoiding possible interfacial recombination

**FETs:** Wires have high e⁻ mobility

Nanowire based DSC

- NW cells are competitive with thin TiO$_2$ nanoparticle cells ($\eta_{cc} \sim 100\%$)
- NW cells outperform ZnO nanoparticle cells

\[ \eta_{PCE} = 1.5\% \text{ under AM 1.5 G conditions} \]

Nanowire DSC

Faster electron injection in NW cell

Bi-exponential (<250fs, 3ps)

vs.

Tri-exponential (<250fs, 20ps, 200ps)
Time Scale for Electron Injection and Transport

Electron injection → Dye regeneration → Electron transport → Interfacial recombination

- Time (s)
  - $10^{-13}$ ps
  - $10^{-11}$ ns
  - $10^{-9}$ μs
  - $10^{-7}$ ms
  - $10^{-5}$ ms
  - $10^{-3}$ ms
  - $10^{-1}$ ms

Loss mechanism: Interfacial recombination

Competition

Electron diffusion length

$L_n = \sqrt{D_n \cdot \tau_n}$

- $D_n$: electron diffusion coefficient
- $\tau_n$: electron lifetime

Grätzel, M, MRS Bulletin, Jan 2005
Engineer active interface to reduce recombination

Core-sheath Nanowire Cells

Overcoat the nanostructured electrode with an insulating or semiconducting oxide

Reduce recombination

- Physically separate electrons and holes
- Form a tunneling barrier
- Passivate recombination centers on oxide surface

Shift band edge to increase $V_{oc}$

- Use an oxide with a higher band edge energy
- Form dipole layer that bends band upwards

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Band Gap (eV)</th>
<th>$E_{VB}$ (eV vs AVS)$^a$</th>
<th>$E_{CB}$ (eV vs AVS)$^a$</th>
<th>Pzc (pH)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>-7.4</td>
<td>-4.19</td>
<td>8.5–9.5</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>3.2</td>
<td>-7.4</td>
<td>-4.21</td>
<td>5.5–6.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.0–9.5</td>
<td>-9.9</td>
<td>-1.6</td>
<td>8.5–9.5</td>
</tr>
</tbody>
</table>

$^a$AVS = Absolute Vacuum Scale. From references 18–20. $^b$The point of zero charge (Pzc) depends on sample preparation, impurities, etc. From references 21–23.

Gregg, B. NREL.
Atomic Layer Deposition (ALD)

**Oxides:** Al$_2$O$_3$, TiO$_2$, Ta$_2$O$_5$, Nb$_2$O$_5$, ZrO$_2$, HfO$_2$, SnO$_2$, ZnO, La$_2$O$_3$, Y$_2$O$_3$, CeO$_2$, Sc$_2$O$_3$, Er$_2$O$_3$, V$_2$O$_5$, SiO$_2$, In$_2$O$_3$, ...

**Perovskites:** SrTiO$_3$, BaTiO$_3$, LiNbO$_3$, LaMnO$_3$ ...

**Nitrides:** AlN, TaN$_x$, NbN, TiN, MoN, ZrN, HfN, GaN, ...

**Fluorides:** CaF$_2$, SrF$_2$, ZnF$_2$, ...

**Metals:** Pt, Ru, Ir, Pd, Cu, Fe, Co, Ni, ...

**Carbides:** TiC, NbC, TaC, ...

**Mixed structures:** AlTiN$_x$, AlTiO$_x$, AlHfO$_x$, SiO$_2$:Al, HfSiO$_x$ ...

**Sulfides:** ZnS, SrS, CaS, PbS, ...

**Nanolaminates:** HfO$_2$/Ta$_2$O$_5$, TiO$_2$/Ta$_2$O$_5$, TiO$_2$/Al$_2$O$_3$, ZnS/Al$_2$O$_3$, ATO (AlTiO) ...

**Doping:** ZnO:Al, ZnS:Mn, SrS:Ce, Al$_2$O$_3$:Er, ZrO$_2$:Y, ... rare earth metals (Ce$^{3+}$, Tb$^{3+}$ etc.) also co-doping

Example: ZnS

Planar Systems, Inc.

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Core-sheath Nanowire Dye-sensitized Solar Cells
Nanowire-polymer Hybrid Cell

Target nanowire array

1) ultrahigh nanowire density
2) short, thin nanowires
3) nanowires normal to substrate

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Nanowire-polymer Composite Film

Aligned wires
Inter-wire spacing is 10-50 nm
$2L_D$ for P3HT $\sim$ 20 nm
Thickness 200-300 nm
The Ideal Nanowire Cell

- Fully interdigitated donor-acceptor interface
- Acceptor wire array: high density, smaller band gap
- Donor: polymer/nanoparticles, maximize absorption
- Interface engineering: reduce recombination.
- Applicable to DSC, hybrid, and conventional semiconductor cells.

N. Lewis

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