High Performance DSSC Based on Semiconducting Oxides Prepared Through Soft Chemistry Processes
Dye-sensitized solar cells
TiO₂, ZnO

Water-splitting oxides
Fe₂O₃, YFeO₃

Electrochromic oxides
WO₃, NiO

Photocatalytic oxides
TiO₂

Li-ion batteries
intercalation materials
LiMn₂O₄, Vanadium oxides,
Li₄Ti₅O₁₂, LiFePO₄, Na₂FePO₄F

Supraconducting oxides
YBa₂Cu₃Oₓ

Magnetoresistive oxides
(La,Ca)MnO₃

Thermoelectric oxides
Misfit cobalt oxides, ZnO

Structural ceramics
Y-ZrO₂, BaZrO₃, mullite,…

Silicon-based photovoltaic panels recycling
RESEARCH TOPICS
www.greenmat.ulg.ac.be

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TiO₂, ZnO

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Fe₂O₃, YFeO₃

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Silicon-based photovoltaic panels recycling

Group of Research in Energy and ENvironment from MATerials
Dye-sensitized solar cells (DSSCs) - Starting point
How do DSSCs work?
GrEEEnMAT expertise area

Research

TiO₂ mesoporous films

ZnO nanorods

5 μm 1 μm 5 μm
Dye-sensitized solar cells (DSSCs) - Starting point
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TiO$_2$ mesoporous films
ZnO nanorods
DYE-SENSITIZED SOLAR CELLS (DSSCs): STARTING POINT


Inspired from the nature...

PHOTOSYNTHESIS

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films

Brian O’Regan* & Michael Grätzel†

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland
DSSCs COMPONENTS

Dye

Semi-conducting oxide (TiO$_2$, ZnO)

Electrolyte

Substrate
glass - polymere - steel
DSSCs ASSEMBLY

Photoelectrode

Conducting substrate

Semiconducting oxide (TiO₂, ZnO)

Dye

Electrolyte

Sealling

Counter-electrode

Conducting substrate + Pt
How do DSSCs work?

www.thesolarspark.co.uk
Dye

Semi-conducting oxide (TiO$_2$, ZnO)

Electrolyte

Substrate
glass - polymere - steel

100 nm 100 nm 100 nm 100 nm 100 nm
Usual DSSCs: TiO$_2$ nanoparticles film

Improvement: Control of the mesostructure TiO$_2$ mesoporous films

GOAL AND STRATEGY
Goal:
Increase of current nanoparticles-based cells efficiency

STRATEGY:
Perfect tuning of the porous network
Pore size
Size and connectivity between crystallites

➔ Improvement of dye and electrolyte infiltration
➔ Increase of the surface area
➔ Enhancement of the electron transfers

Improvement:
Control of the mesostructure TiO$_2$ mesoporous films
Goal:
Increase of current nanoparticles-based cells efficiency

**STRATEGY:**
Perfect tuning of the porous network
Nanorods alignment

- Improvement of dye and electrolyte infiltration
- Increase of the surface area
- Enhancement of the electron transfers

Improvement:
Control of the mesostructure ZnO nanorods
Presentation overview

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Dye-sensitized solar cells (DSSCs) - Starting point
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SYNTHESIS PROCESS: TEMPLATING

2 Processes:

1) EISA (Evaporation Induced Self-Assembly)

2) EIMP (Evaporation Induced Micelles Packing)
SYNTHESIS PROCESS: TEMPLATING

SOLVENT, $\text{H}_2\text{O}, \text{HCl} \uparrow$
MICELLES ORGANISATION

INORGANIC CONDENSATION

$\Delta T$
SURFACTANT $\uparrow$
PORE MERGING AND CRYSTALLISATION
## Influence of the Structuring Agent

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>F127</th>
<th>P123</th>
<th>PSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular structure</td>
<td>(\text{PEO}<em>{106}\text{PPO}</em>{70}\text{PEO}_{106})</td>
<td>(\text{PEO}<em>{20}\text{PPO}</em>{70}\text{PEO}_{20})</td>
<td>(\text{PS}<em>{16400}\text{PEO}</em>{36400})</td>
</tr>
<tr>
<td>Hydrophobic part ↔ Pore size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>4-6</td>
<td>5-7</td>
<td>19-21</td>
</tr>
</tbody>
</table>
Influence of the Relative Humidity (RH)

Low RH  \(\rightarrow\)  High RH

50 nm

Wormlike  \(\rightarrow\)  Gridlike
Mesostructure  Mesostructure

Henrist C., Dewalque J., Mathis F., Cloots R.; *Micro Meso Mat*, 2009, 117 (1–2), 292
SYNTHESIS PROCESS: TEMPLATING

SOLVENT, 
H₂O, HCl →
MICELLES 
ORGANISATION

RH ↗ = slower evaporation → Micelles organisation ↗

INORGANIC 
CONDENSATION

ΔT
SURFACTANT ↗
PORE MERGING AND 
CRYSTALLISATION
4h 600°C

Collapsed mesostructure

2h 350°C

Preserved mesostructure

INFLUENCE OF THERMAL TREATMENT
PORE CONNECTIVITY PRESERVATION
AT 350°C (2H)
BY 3D TOMOGRAPHY
Monolayer film only between 100-300 nm thick
  = low developed surface
  = low amount of adsorbed dye (active material)

→ Need to increase the film thickness
→ Tuning of a multilayer deposition process
Repeated thermal treatments can induce the mesostructure degradation

- Surface area limitation
DEPOSITION

STABILISATION

15min 300°C

Stabilisation
• Solvents and volatile species evaporation
• Inorganic network condensation

Calcination
• Surfactant elimination and pores merging
• Anatase crystallisation

MULTILAYER AND REPEATED THERMAL TREATMENTS

2h 350°C
1°C/min
MULTILAYER AND REPEATED THERMAL TREATMENTS

Limitation of the surface area increase
Zukalova et al., *Nano Letters* 2005, 5, (9), 1789-1792

$\to (SC)^n$ thermal scheme
Calcination every layer

$\to (SSSC)^{n/3}$ scheme
Calcination every $\mu m$

Limitation of the mesostructure collapse
Linear increase of the surface area
High crystallinity

Pore filling during the subsequent deposition steps

Partial or full elimination of the structuring agent
⇒ Risk of pore filling

⇒ Surface area decrease
<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of layer</th>
<th>Film thickness (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F127 wormlike</td>
<td>1 layer</td>
<td>235</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>3 layers</td>
<td>645</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>5 layers</td>
<td>1075</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>1 layer</td>
<td>110</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>3 layers</td>
<td>300</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>5 layers</td>
<td>500</td>
<td>35.5</td>
</tr>
<tr>
<td></td>
<td>10 layers</td>
<td>955</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1 layer</td>
<td>320</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>3 layers</td>
<td>890</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>5 layers</td>
<td>1560</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>1 layer</td>
<td>380</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>3 layers</td>
<td>1030</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>5 layers</td>
<td>1820</td>
<td>44</td>
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<td>31.5</td>
<td>2.2 x 10⁻⁴</td>
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<td>1.4 x 10⁻⁴</td>
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<tr>
<td>P123 gridlike, 1 µm</td>
<td>44</td>
<td>3.0 x 10⁻⁴</td>
</tr>
<tr>
<td>Nanopart. reference, 3.5 µm</td>
<td>/</td>
<td>1.1 x 10⁻⁴</td>
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P123 better than F127

Pore filling

No pore filling

MULTILAYER FILMS ➔ 1µm
## Multilayer Films → 1µm

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Wormlike better than gridlike
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**Best DSSC candidate**
Templating allows improving DSSC efficiency

After 2 weeks ageing

COMPARISON WITH OTHER TEMPLATED FILMS FROM THE LITERATURE

• High surface area ➔ High dye loading, even for thin layer (Optimal film thickness for solid-state DSSCs = 2µm)

• Perfect control of the film mesostructure and highly connected pores ➔ Facilitated solid electrolyte infiltration
Hierarchical porous structure for solid-state DSSC applications

Combined Soft and Hard templating

Surfactant

Ti precursor

Solid sphere

Hierarchical porous structure for solid-state DSSC applications

- Thick layers prepared from one-pot process
- Higher thickness
- Accessible and ordered pores
- Facilitated solid electrolyte infiltration (big pores)
- High surface area (small pores)

Dye-sensitized solar cells (DSSCs) - Starting point
How do DSSCs work?
GrEEEnMAT expertise area
Spin coating of ZnO seeds → ZnO nanorods hydrothermal growth → Dye impregnation and cell assembly

ZnO nanorods

Liquid electrolyte or hole conductor

Pt/F:SnO$_2$/glass

F:SnO$_2$/glass

Load

Light

5 µm

7.8 $10^{13}$ wires/m$^2$
**INCREASE OF THE FILM SURFACE AREA AND PORE ACCESSIBILITY \(\rightarrow\) HARD TEMPLATING**

**Templated Growth (TG)**

1. Spin coating of colloidal suspension
2. Hydrothermal growth
3. \(\Delta T\)
4. Seed layer, PS nanosphere, ZnO nanowire, FTO substrate

**Surface area**

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<tr>
<th>Sample</th>
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<tr>
<td>Templated</td>
<td>(2.43 \times 10^{-10})</td>
</tr>
<tr>
<td>Untemplated</td>
<td>(1.68 \times 10^{-10})</td>
</tr>
</tbody>
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**Higher efficiencies for templated cells**

GrEEnMat Team

DSSC team
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Thank you for your attention

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