Repeated thermal treatments applied to ordered TiO$_2$ mesoporous thin film: effect on the film crystallization and surface area

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Effect of Repeated heat treatment on TiO$_2$ mesoporous thin films

OUTLINE

• INTRODUCTION
  – Why such a study?

• EXPERIMENTAL PART
  – How to prepare the films?

• RESULTS
  – Mesostructure (TEM)
  – Crystallinity (XRD)
  – Porosity & Surface area (EEP)
  – PV efficiency (IV)

• CONCLUSIONS
  – What matters most?
Introduction: why study ordered mesoporous films?

Anatase mesoporous thin film

Photo Electrode

Electrons migrating through the film

Light

Dye

Electrolyte

Counter-electrode

Motor
Classical nanocrystalline film

Controlled porous network

- Controlled & Homogeneous porosity
- Monodisperse crystal size
- Ordered TiO$_2$ network
- Facilitates pore filling and electron conduction in TiO$_2$
HOW TO PREPARE ORDERED MESOPOROUS THIN FILMS?

IN SOLUTION (ButOH) MICELLIZATION

NON POLAR POLAR

SELF-ASSEMBLING

AFTER DEPOSITION INORGANIC POLYMERIZATION

EVAPORATION-INDUCED MICELLE PACKING

Evaporation of ButOH and HCl

THERMAL TREATMENT
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EXPERIMENTAL PART
Experimental details

- 1-butanol
- Pluronic P123
- Ti-(iPrO)₄
- HCl conc.

**Evaporation of**

- $\text{H}_2\text{O}$, ButOH and HCl
- 0.8 mm/s
- HR = 25%
- 15’ @ 300°C

**Stabilization**
- Evaporation of solvent and by-product
- Condensation of inorganic network

**Calcination**
- Full removal of micelles
- Further condensation of TiO₂
- Crystallization & Crystal growth

- 2H @ 350°C
- 1°C/min
Experimental details

- 1-butanol
- Pluronic P123
- Ti-(iPrO)₄
- HCl conc.

Evaporation of \( \text{H}_2\text{O}, \text{ButOH and HCl} \)

0.8 mm/s

HR = 25%

15' @ 300°C

STABILIZATION

Stabilization
- Evaporation of solvent and by-product
- Condensation of inorganic network

Calcination
- Full removal of micelles
- Further condensation of TiO₂
- Crystallization & Crystal growth
MULTILAYERS DEPOSITION

Layer 1 → Layer 2 → Layer 3 → ….

→ \((SC)^n\) scheme
Calcination after each layer

→ \((SSSC)^{n/3}\) scheme
Calcination every 3 layers

Surface area limitation
Zukalova et al., *Nano Letters* 2005, 5, (9), 1789-1792

Preservation of open porosity???
High surface area?
AIM OF THE STUDY: effect of repeated thermal treatment on a single layer

- How will the first layer in a multilayer film be influenced by repeated thermal treatment?
- How to limit degradation of porosity?
- How to optimize crystallization of anatase?
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RESULTS
Figure 1: TEM micrographs of monolayer films after different thermal schemes.

1. MESOSTRUCTURE & ORDER

- (SC)\(^1\) Open wormlike (+ destroyed)
- (SC)\(^3\) Destroyed
- (SSSC)\(^1\) Open wormlike
- (SSSC)\(^4\) Destroyed
- (SC)\(^{12}\) Destroyed

50 nm
2. THICKNESS & SURFACE AREA

Figure 2: Evolution of the film thickness (up) and surface area (bottom) with the number of stabilization steps.

Stabilization steps reduce/delay film contraction, increases mechanical resistance.

Stabilization steps delay the arising of surface area plateau.
2. THICKNESS & SURFACE AREA

**Figure 2:** Evolution of the film thickness (up) and surface area (bottom) with the number of stabilization steps.

Stabilization steps reduce/delay film contraction, increases mechanical resistance.

Is (SSSC)\(^1\) the most porous sample?
3. CRYSTAL SIZE & CRYSTALLINITY

Figure 3: Evolution of the crystallite size with the number of stabilization steps. Horizontal dashed line: limit of crystal size inducing mesostructure collapsing.

Partly destroyed

Open wormlike

limit before collapse = 7,8 nm

number of stabilization steps

crystallite size (nm)
3. CRYSTAL SIZE & CRYSTALLINITY

Two samples contain open wormlike porosity

Preserved wormlike porosity implies low crystallinity

*Area of Anatase [101] peak

**Crystallinity (a.u.)*

- (SC)\(^n\)
- (SSSC)\(^{n/3}\)

**Crystallite size (nm)**

- (SC)\(^1\)
- (SSSC)\(^1\)
- (SC)\(^3\)
- (SSSC)\(^2\)
- (SC)\(^6\)
- (SSSC)\(^3\)
- (SC)\(^9\)
- (SSSC)\(^4\)
- (SC)\(^12\)

**Limit of collapsing**

- (SC)\(^1\)
- (SSSC)\(^1\)
- (SC)\(^3\)
- (SSSC)\(^2\)
- (SC)\(^6\)
- (SSSC)\(^3\)
- (SC)\(^9\)
- (SSSC)\(^4\)

**Number of stabilization steps**

<table>
<thead>
<tr>
<th>SC</th>
<th>SSSC</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
</tr>
</tbody>
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**Film crystallinity (a.u.)**

- (SC)\(^1\)
- (SC)\(^3\)
- (SC)\(^6\)
- (SC)\(^9\)
- (SC)\(^12\)

- (SSSC)\(^1\)
- (SSSC)\(^2\)
- (SSSC)\(^3\)
- (SSSC)\(^4\)
4. ASSEMBLY & PV TESTING

- THERMAL TREATMENT
- DYEING
- ASSEMBLING & SEALING
4. ASSEMBLY & PV TESTING

Cell area: 0.2064 cm$^2$
Dye: N719 (Dyesol)
FTO: 15 $\Omega$ sq + 30 nm Pt
Electrolyte: EL-HSE (Dyesol)
Illumination: 1 sun, AM1.5

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Thick. (nm)</th>
<th>Open worm-like</th>
<th>Surf. Area* (m$^2$/cm$^3$)</th>
<th>Crystal-linity (a.u)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SC)$^1$</td>
<td>335</td>
<td>YES</td>
<td>198</td>
<td>44</td>
</tr>
<tr>
<td>(SC)$^3$</td>
<td>330</td>
<td>NO</td>
<td>189</td>
<td>52</td>
</tr>
</tbody>
</table>

* Pore radius > 2nm
** Anatase [101] peak area
4. ASSEMBLY & PV TESTING

Cell area: 0.2064 cm²
Dye: N719 (Dyesol)
FTO: 15 Ω/sq + 30 nm Pt
Electrolyte: EL-HSE (Dyesol)
Illumination: 1 sun, AM1.5

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Thick. (nm)</th>
<th>Open worm-like</th>
<th>Surf. Area (m²/cm³)</th>
<th>Crystal-linity (a.u)</th>
<th>Voc (mV)</th>
<th>Isc (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
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<tr>
<td>(SC)¹</td>
<td>335</td>
<td>YES</td>
<td>198</td>
<td>44</td>
<td>710</td>
<td>1.35</td>
<td>0.69</td>
<td>0.71</td>
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<td>(SC)³</td>
<td>330</td>
<td>NO</td>
<td>189</td>
<td>52</td>
<td>749</td>
<td>1.46</td>
<td>0.71</td>
<td>0.83</td>
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Conclusions
What matters most?
1. MICROSTRUCTURE FEATURES

• Wormlike Mesostructure is destroyed after 2nd calcination (crystal size > 7,8nm)
• (SC)\textsuperscript{n} films are more crystallized than (SSSC)\textsuperscript{n}
• Stabilization steps (15’@300°C)
  – Allows multilayer deposition
  – Delays Nucleation & crystal growth
  – Delays mesostructure collapse
  – Reduces film contraction
  – influences the development of the porosity upon calcination
  – Helps keeping high surface area
2. PV PERFORMANCES

• Microporosity does not contribute to PV performances (pore $\phi<4$ nm)

• Open, wormlike porosity is NOT a critical parameter

• Crystallinity exerts a strong influence on PV efficiency (maybe more than surface area)
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THANK YOU FOR YOUR ATTENTION