Place of TiO$_2$ in organic and dye sensitized solar cells: General overview

Canan VARLIKLI

Ege University, Solar Energy Institute, Bornova –İzmir /TÜRKİYE
www.eusolar.ege.edu.tr
canan.varlikli@ege.edu.tr
A search in Web of Science for the key words of “TiO$_2$ and energy” in topic approx. 15.000 publications, 80% published between 2003-2013.

Number of publications vs years for the key words of “TiO$_2$ and energy” according to Web of Science.

Relative distribution of publications on focused application areas of TiO$_2$ in energy topic, according to Web of Science.
TiO$_2$ in Solar Cell

A solar cell converts solar energy into electricity.

The most common photovoltaic material is silicon (Si).

Production costs are the major handicap of Si-based photovoltaics.

The potential of TiO$_2$ films to reduce the production costs has been investigated extensively.

Depending on the cell design, TiO$_2$ could serve in multiple purposes*;

- reflection coating,

Refractive index mismatching between TCO layer ($n \approx 1.9$ for SnO2) and Si ($n \approx 3.5$) causes reflection/optical losses. Modification of TCO surfaces with anti-reflective coatings, reduce the reflection losses and increase the trapping of light. TiO$_2$ ($n \approx 2.5$) is one of the widely used antireflective layers.

TiO$_2$ in energy conversion: Solar Cell

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• reflection coating,

• surface passivation,

• diffusion barrier (optical spacer)

thin layers of TiO$_2$ and SiO$_x$ optical layers have been applied to the a-Si/µc-Si solar cells

SiO$_x$ films have been grown by PECVD technique

TiO$_2$ thin films have been developed by RF-magnetron sputtering of TiO$_2$:Nb$_2$O$_5$ targets

The device structure of
glass/ZnO(texture-etched)/TiO$_2$/ZnO(10nm)/a-Si(p–i–n)/n-SiO$_x$/µc-Si(p–i–n)/ZnO–Ag
gave 11.8% conversion efficiency

4.42% enhancement by using TiO$_2$ anti-reflection layer between the TCO/Si interface
Photovoltaic performance of this hybrid system was related to the photodegradation of organic pollutant (methylene blue-MB dye)
The use of TiO$_2$ is more attractive in dye sensitized solar cells (DSSCs)

- 3$^{rd}$ generation PV technology developed by O’Regan and Gratzel in 1991*.
- Since the first reviews on DSSCs** literature has gained more than 90 additional review articles. The reason of this enormous attention is their environmental friendly properties, low costs, and device flexibility they provide.
- DSSC technology has made important progress in commercialization as well ***

Some other metal oxide SCs such as Nb$_2$O$_5$, ZnO, SnO$_2$, WO$_3$, CeO$_2$, and NiO have also been investigated but the obtained conversion efficiencies were far below TiO$_2$.

**What is so special about TiO$_2$?**

- Large SSA,
- large porosity,
- rapid electron transport,
- low electron recombination and
- good electronic contact between TiO$_2$ film and TCO glass.

Generally small TiO$_2$ nanoparticles with 10-50 nm particle sizes are used. Although small particle sizes provide large SSA for adsorption of the dye, they cannot benefit from incident light due to their transparency.

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In order to enhance light harvesting efficiency incorporating large particles and some porous structures in TiO₂ as antireflective multilayers or deposition of some large particle layers on photoelectrode has been studied. Zhang et al. * have used combination of TiO₂ nanoparticles with anatase TiO₂ hollow spheres that provided effective light scattering. The reference device was with P25:

- Controlled both the concentration and thickness.

Increasing the concentration increased the back light scattering. A thickness of 14.2 μm exhibited the highest performance of 7.59%, much higher than the performance of DSSC with P25 photoanode of 11 μm (6.67%).

Wu et al. ** employed shell-in-shell TiO₂ (S@S-TiO₂) hollow spheres as the light scattering layer over the P25 film and tuned the thickness of each layer. The P25(11 μm)/S@S-TiO₂(5 μm) bilayer structure gave an efficiency of 9.10% where that of bare P25 TiO₂ photoanode could reach 7.65%.

* J. Mater. Chem. Phys. 2010, 123, 595-600
** Energy Environ. Sci., 2011, 4, 3565-3572
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In order to enhance charge transport properties, TiO$_2$ nanostructures have been used with single walled carbon nanotubes (SWCNTs), and graphene.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>J$_{sc}$</th>
<th>V$_{oc}$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure P25 (10µm/15µm)</td>
<td>11.9/14.9</td>
<td>683/711</td>
<td>4.96/6.25</td>
</tr>
<tr>
<td>GSCT-P25 (10µm)</td>
<td>14.6</td>
<td>696</td>
<td>6.46</td>
</tr>
<tr>
<td>P25-GTNTs (15µm)</td>
<td>18.3</td>
<td>742</td>
<td>7.54</td>
</tr>
<tr>
<td>GSCT-P25-GNTNTs (15µm)</td>
<td>21.3</td>
<td>741</td>
<td>8.67</td>
</tr>
</tbody>
</table>

GTNT graphene modified titanate nanotube
GSCT graphene and TiO$_2$

(a) TEM images of the pure TNTs, the inset shows the high magnification image;
(b) TEM image of the SCT, monolayer TiO$_2$ and TiO$_2$ nanoparticle are marked.

J. Power Sources, 2012, 220, 95-102
Anionic and cationic species have also been tried as dopants in TiO₂ based photoanodes. Nitrogen attracts much attention due to their enhanced visible light absorption abilities...

10.1% efficiency has been achieved by Guo et al. *.* The higher efficiency obtained was due to higher dye uptake ability, faster electron transport and higher photovoltage effect of N-TiO₂ films.

<table>
<thead>
<tr>
<th>Titania electrode</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped ST-01</td>
<td>778 ± 10</td>
<td>19.05 ± 0.07</td>
<td>0.68 ± 0.01</td>
<td>10.1 ± 0.2</td>
</tr>
<tr>
<td>Undoped ST-01</td>
<td>756 ± 13</td>
<td>17.40 ± 0.10</td>
<td>0.68 ± 0.01</td>
<td>8.9 ± 0.3</td>
</tr>
<tr>
<td>S-ST-01</td>
<td>700 ± 10</td>
<td>12.30 ± 0.10</td>
<td>0.65 ± 0.01</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>Commercial ST-01</td>
<td>741 ± 15</td>
<td>6.66 ± 0.03</td>
<td>0.56 ± 0.01</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>N-doped P25</td>
<td>789 ± 10</td>
<td>14.66 ± 0.13</td>
<td>0.69 ± 0.01</td>
<td>8.0 ± 0.2</td>
</tr>
<tr>
<td>Commercial P25</td>
<td>769 ± 15</td>
<td>13.58 ± 0.07</td>
<td>0.68 ± 0.01</td>
<td>7.1 ± 0.2</td>
</tr>
<tr>
<td>N-doped A</td>
<td>784 ± 8</td>
<td>15.58 ± 0.17</td>
<td>0.68 ± 0.01</td>
<td>8.3 ± 0.3</td>
</tr>
<tr>
<td>Undoped A</td>
<td>747 ± 7</td>
<td>14.80 ± 0.17</td>
<td>0.65 ± 0.01</td>
<td>7.2 ± 0.3</td>
</tr>
</tbody>
</table>

But one has to keep in mind that the N-doping level and consequent positive effects on DSSC performance depends on the nature of nitrogen source**

Zn, Cr, Nb, La, Ta, Sb, Ag and Al-W have been used as cationic dopants in TiO₂

higher electron injection efficiency from LUMO of dye to the CB of TiO₂ due to the positive shifted flat band potential and fast electron transport rate resulting from reduced film resistance...***

**Energy 36 (2011) 1243-1254
Lei et al. achieved 8.1% efficiency by using anatase nc-TiO$_2$ nanotube arrays on FTO substrate with relative high SSA benefiting from relatively long nanotube length of 20.8 µm ***.

Adachi et al. ** reported 9.3% conversion efficiency for a DSSC that include single-crystal-like TiO$_2$ nanowire based photoanode.

HRTEM image of several titania nanowires with single anatase structure formed by oriented attachment. Arrows in the HRTEM image indicate the indentations.

** J. Am. Chem. Soc. 2004, 126, 14943-149949
TiO_2 in organic solar cells

The CB energy level of TiO_2 provides its usage as an optical spacer, i.e. lower than the LUMO of most of the polymeric SCs and close to the Fermi energy level of metallic electrode. The addition of an optical spacer between the active layer and metal electrode increases the number of excitons formed.

The use of TiO$_2$ as an ETL in organic/inorganic hybrid OPV devices is more common.*

The morphologies of TiO$_2$ structures that are used in OPV applications may vary from particle to nanorod and nanotube, the trend is on ordered structures.

(a,b) The top view SEM images of ZnO nanorods and TiO$_2$ nanotubes, respectively, (c) the schematic process of preparing TiO$_2$ nanotubes, and (d) the cross section of hybrid solar cell photoelectrode using TiO$_2$ nanotubes.

FESEM image of a mechanically fractured 4 µm long TiO$_2$ nanotube array sample.


*** Langmuir 2007, 23, 12445-12449
Why?
How?
What?

- *Prog. in Photovol.: Res. and Appl.* 2012, 20, 698-710
Thanks For Your Attention