Place of TiO_2 in organic and dye sensitized solar cells: General overview

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PV Systems Engineering & the other Renewable Energy Systems
through the Entrepreneurship spirit
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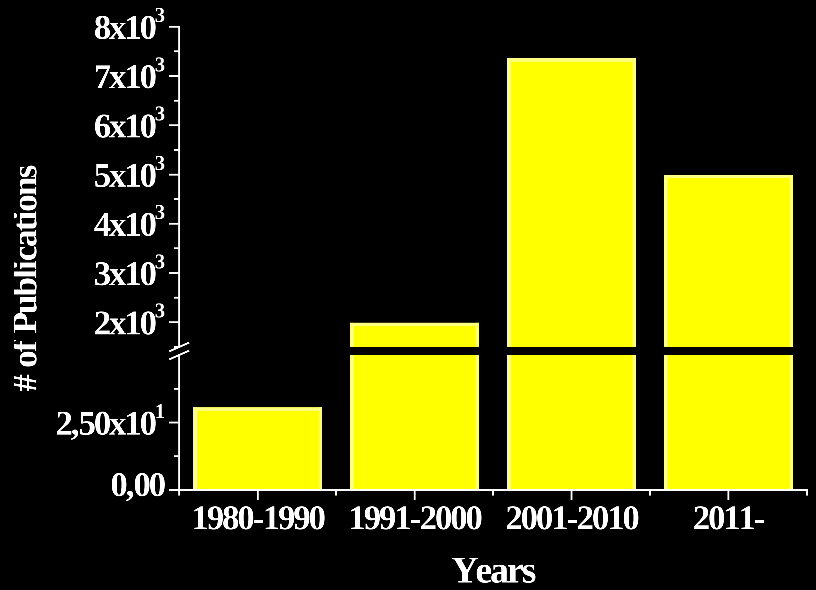
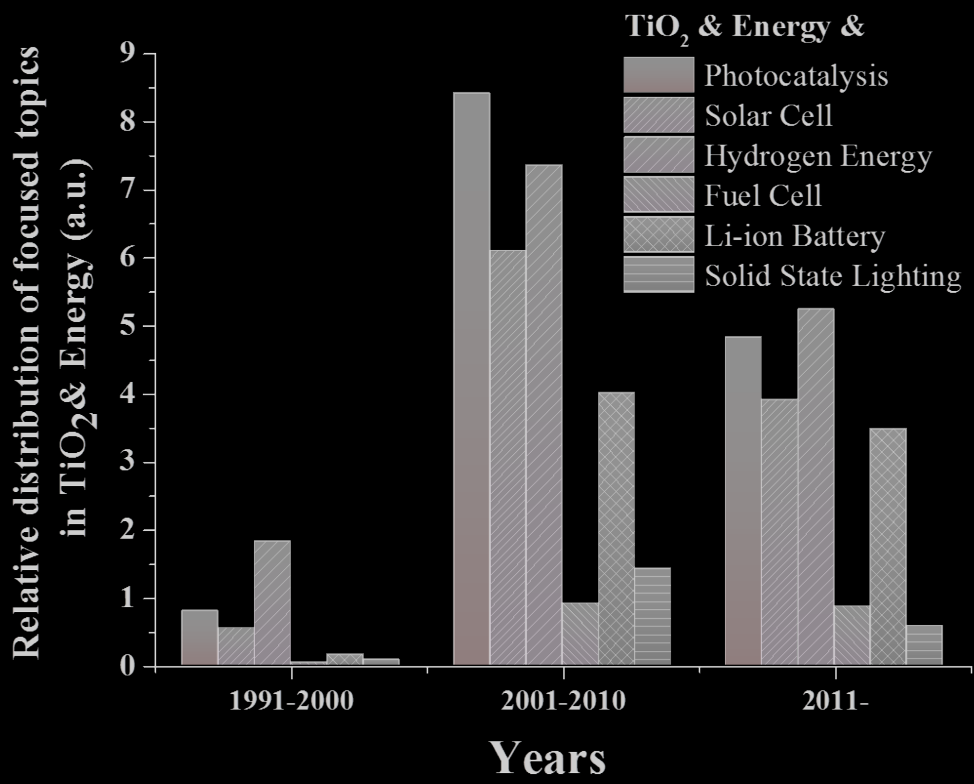
A search in Web of Science for the key words of "TiO_2 and energy" in topic
approx. 15.000 publications, 80% published between 2003-2013



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 ($n\approx1.9$ for SnO2) and Si ($n\approx3.5$) causes reflection/optical losses. Modification of TCO surfaces with anti-reflective coatings, reduce the reflection losses and increase the trapping of light. TiO_2 ($n\approx2.5$) is one of the widely used antireflective layers

Prog. in Photovol.: Res. and Appl. 2004, *12*, 253-281; Solar En. Mater. Solar Cells 2012, 105, 317-321

TiO_2 in energy conversion: Solar Cell

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Production costs are the major handicap of Si based photovoltaics.

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Depending on the cell design, TiO_2 could serve in multiple purposes*;

- reflection coating,
- surface passivation,
- diffusion barrier (optical spacer)

*_Prog. in Photovol.: Res. and Appl._ 2004, _12_, 253-281; Solar En. Mater. Solar Cells 2012, 105, 317-321

Solar Energy Materials & Solar Cells 93 (2009) 973–975

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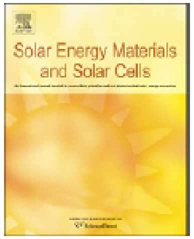


Performance of superstrate multijunction amorphous silicon-based solar cells using optical layers for current management

Chandan Das *, Alain Doumit, Friedhelm Finger, Aad Gordijn, Juergen Huepkes, Joachim Kirchhoff, Andreas Lambertz, Thomas Melle, Wilfried Reetz

IEF5-Photovoltaik, Forschungszentrum Juelich GmbH, Leo-brandt str., 52425 Juelich, Germany

thin layers of TiO_2 and SiO_x optical layers have been applied to the a-Si/μc-Si solar cells

SiOx films have been grown by PECVD technique

TiO_2 thin films have been developed by RF-magnetron sputtering of TiO_2:Nb_2O_5 targets

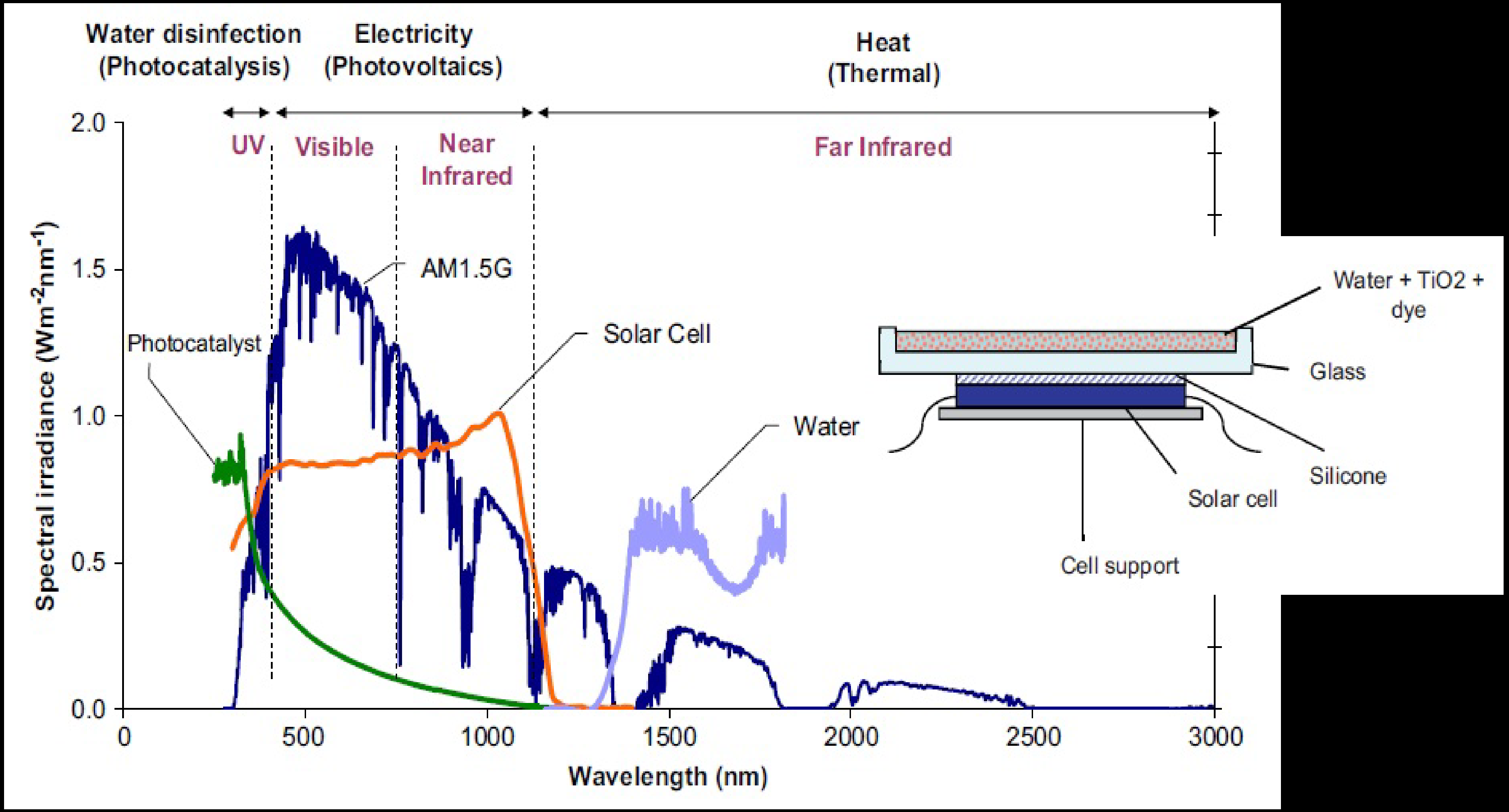
The device structure of

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

Vivar et.al., First lab-scale experimental results from a hybrid solar water purification and photovoltaic system, Solar Energy Materials & Solar Cells 98 (2012) 260–266



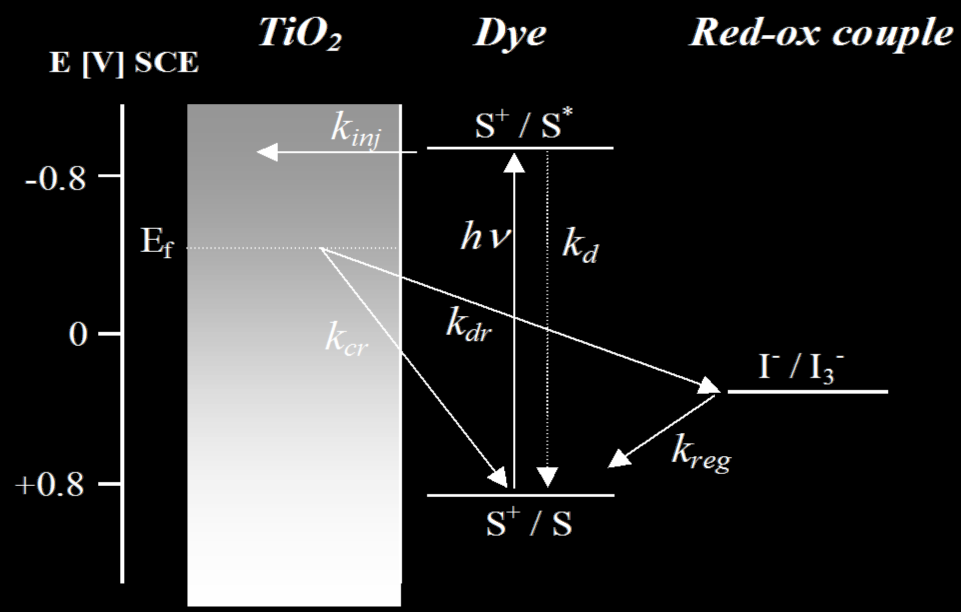
Photovoltaic performance of this hybrid system was related to the

photodegradation of organic pollutant (methylene blue-MB dye)

The use of TiO_2 is more attractive in **dye sensitized solar cells** (DSSCs)

- 3rd 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 ***

The used photoanode influences the performance due to their light harvesting, electron injection-collection and unwanted electron recombination effects



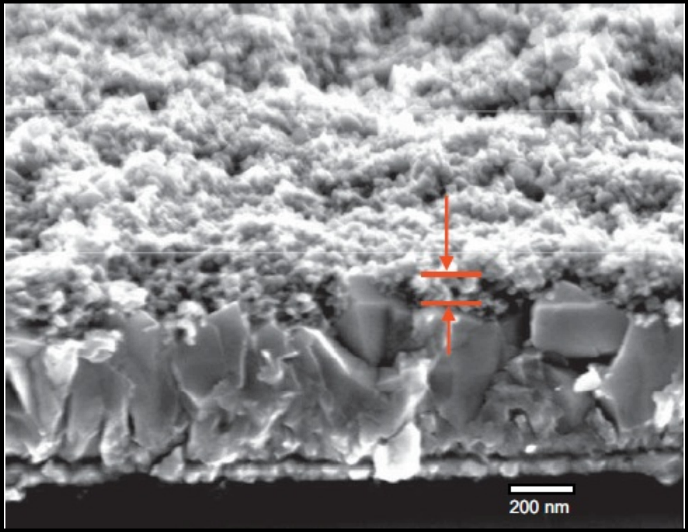
* *Nature* 1991, *353*, 737-740.
*******J. Electroceramics* 1997, *1*, 239-272.; *Coord. Chem. Rew.* 1998, *177*, 347-414; *Res. Chem. Inter.* 2000, *26*, 145-152.; *J. Photochem. Photobiol. C: Photochem. Rev.* 2003, *4*, 145-153.
*** *Prog. in Photovol.: Res. and Appl.* 2012, 20, 698-710.; *Solar En. Mater. Solar Cells* 2012, 102, 109-113; *Solar En. Mater. Solar Cells* 2012, 98, 417-423.

Some other metal oxide SCs such as Nb_2O_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 **



A cross sectional image of the monolayer TiO_2 film coated on FTO glass ***

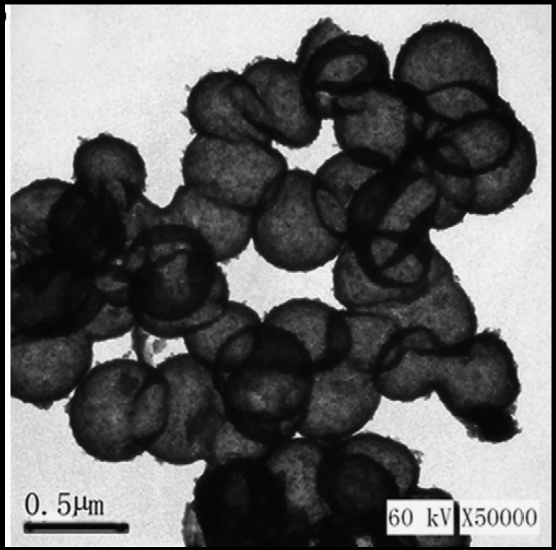
J. Photochem. Photobiol. A: Chem. 2011, *219*, 180-187; *Angew. Chem. Int. Ed*. 2008, *47*, 2402-2406; *Adv. Mater.* 2009, *21*, 3663-3667; *Adv. Mater*. 2009, *21*, 2993-2996; *Nanotechnology* 2008, *19*, 295304-295313.
****J. Phys. Chem. B** 2006, 110, 15932-15938
***Solar En. Mater. Solar Cells* 2010, 94, 686-690

In order to enhance light harvesting efficiency incorporating large particles and some porous structures in TiO_2 as antireflective multilayers or deposition of some large particle layers on photoelectrode has been studied

Zhang *et al.* * have used combination of TiO_2 nanoparticles with anatase TiO_2 hollow spheres that provided effective light scattering

ref device was with P25

- Controlled both the concentration and
- thickness

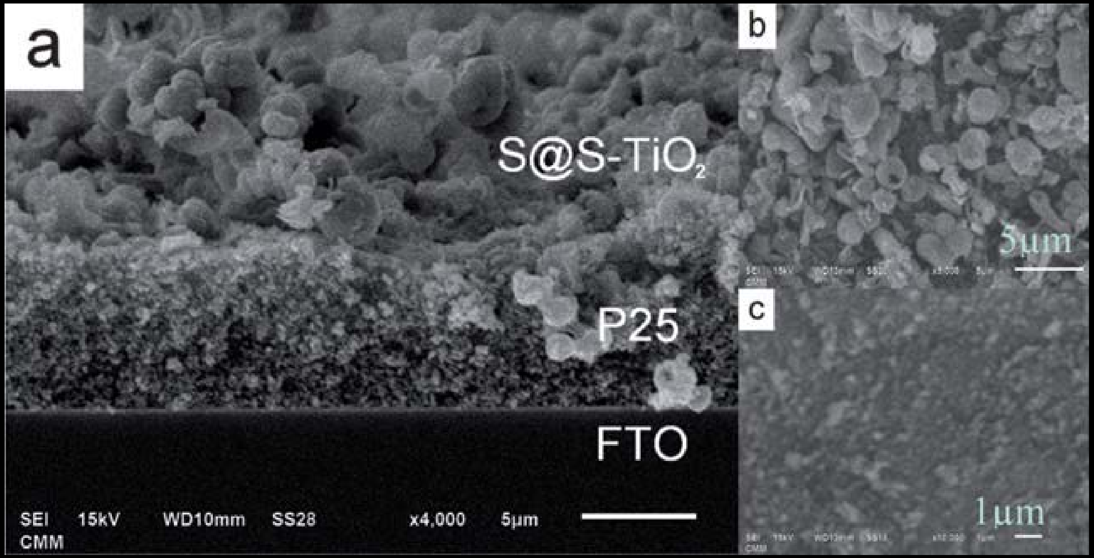


Increasing the concentration, Increased the back light scattering

thickness of 14.2μm exhibited the highest performance of 7.59%, much higher than the performance of DSSC with P25 photoanode of 11μm (6.67%).

Wu *et al.*** employed shell-in-shell TiO_2 (S@S-TiO_2) hollow spheres as the light scattering layer over the P25 film and tuned the thickness of each layer.

P25(11μm)/S@S-TiO2(5μm) 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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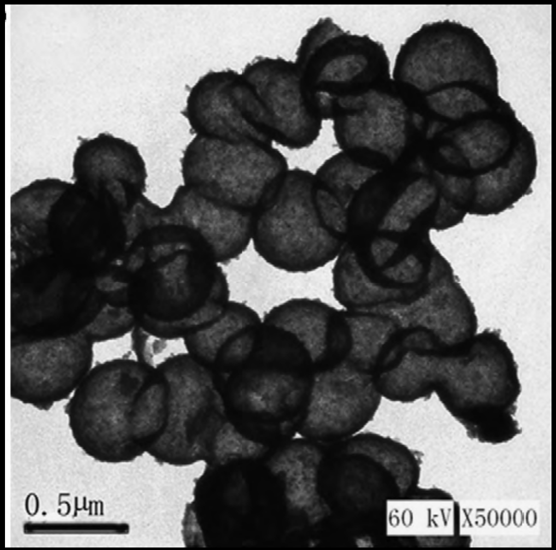

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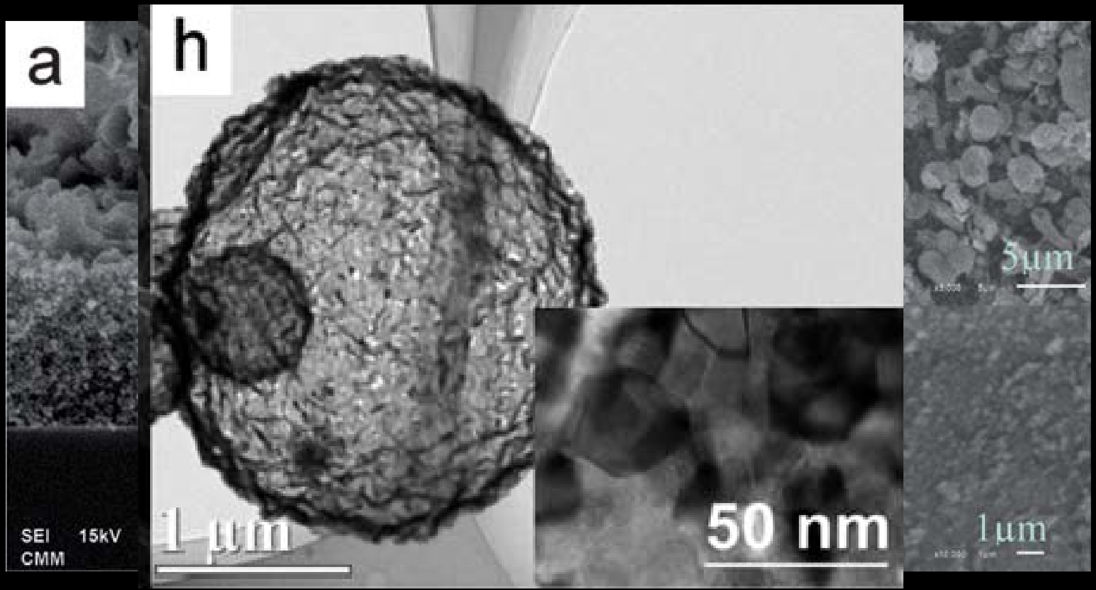
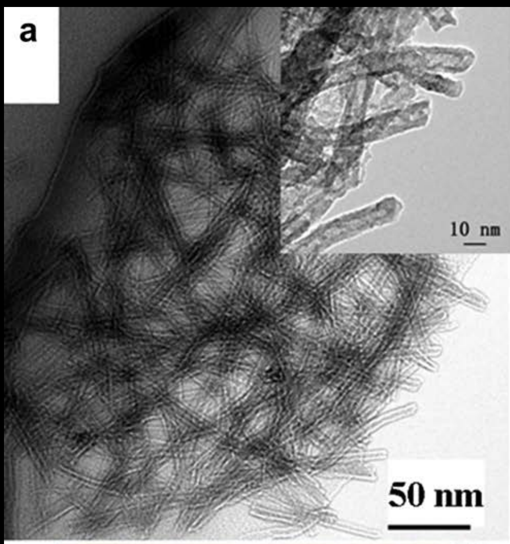


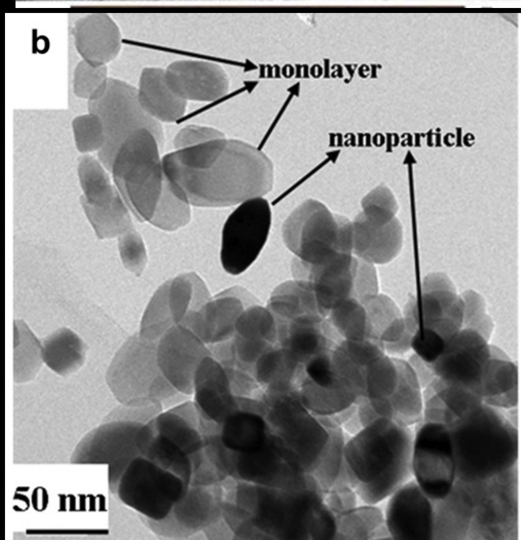
* J. *Mater. Chem. Phys.* 2010, *123*, 595-600

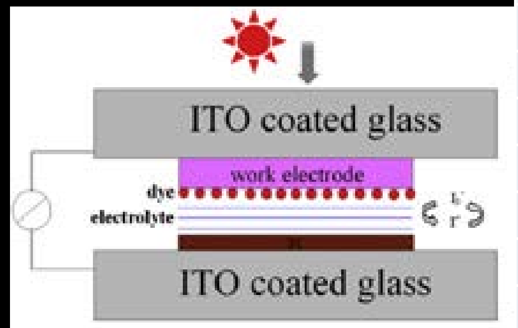
**Energy Environ. Sci., 2011, 4, 3565-3572

In order to enhance charge transport properties, TiO_2 nanostructures have been used with single walled carbon nanotubes (SWCNTs), and graphene

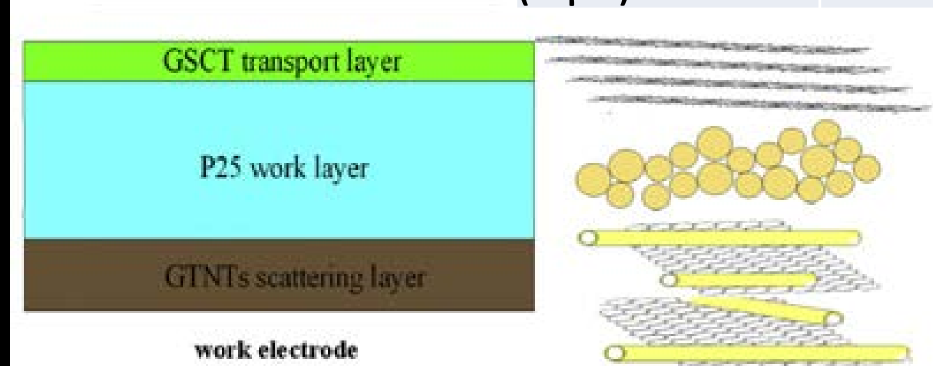
GTNT graphene modified titanate nanotube
GSCT graphene and TiO2



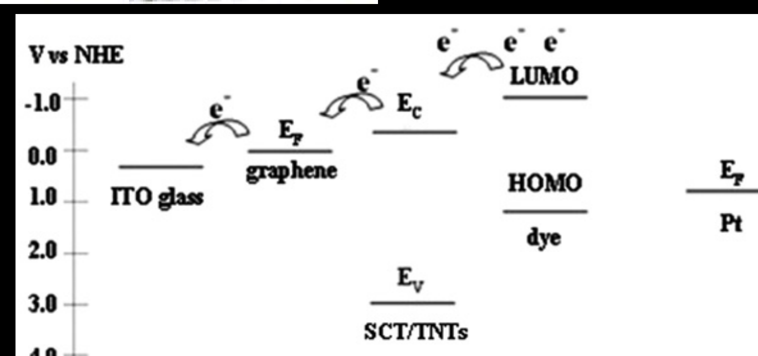




Photoanode	Jsc	Voc	η (%)
pure P25 (10μm/15μm)	11.9/14.9	683/711	4.96/6.25
GSCT-P25 (10μm)	14.6	696	6.46
P25-GTNTs (15μm)	18.3	742	7.54
GSCT-P25-GNTNTs (15μm)	21.3	741	8.67



(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 TiO_2 based photoanodes.

N, S, C, B, P, I, F

nitrogen attracts much attention due to their enhanced visible light absorption abilities…

Table 1
Performance of the DSCs based on the N-doped and undoped TiO_2 electrodes using organic electrolyte solution.

Titania electrode	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
N-doped ST-01	778 ± 10	19.05 ± 0.07	0.68 ± 0.01	10.1 ± 0.2
Undoped ST-01	756 ± 13	17.40 ± 0.10	0.68 ± 0.01	8.9 ± 0.3
S-ST-01	700 ± 10	12.30 ± 0.10	0.65 ± 0.01	5.6 ± 0.2
Commercial ST-01	741 ± 15	6.66 ± 0.03	0.56 ± 0.01	2.7 ± 0.2
N-doped P25	789 ± 10	14.66 ± 0.13	0.69 ± 0.01	8.0 ± 0.2
Commercial P25	769 ± 15	13.58 ± 0.07	0.68 ± 0.01	7.1 ± 0.2
N-doped A	784 ± 8	15.58 ± 0.17	0.68 ± 0.01	8.3 ± 0.3
Undoped A	747 ± 7	14.80 ± 0.17	0.65 ± 0.01	7.2 ± 0.3

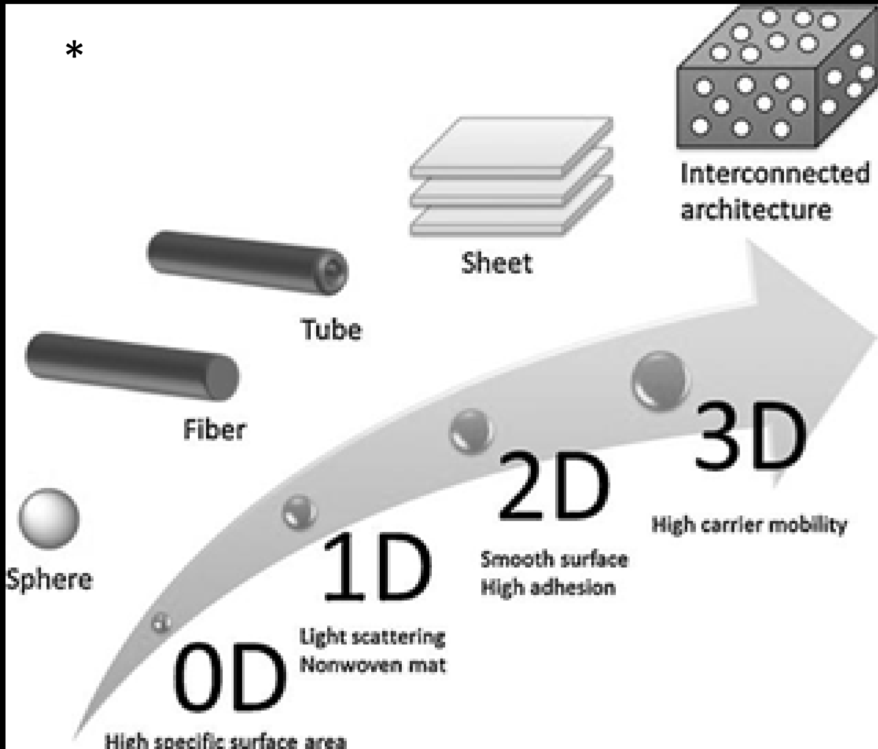
10.1% efficiency has been achieved by Guo et al. *. The higher efficiency obtained was due to
higher dye uptake ability, faster electron transport and
higher photovoltage effect of N-TiO_2 films.

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 TiO_2

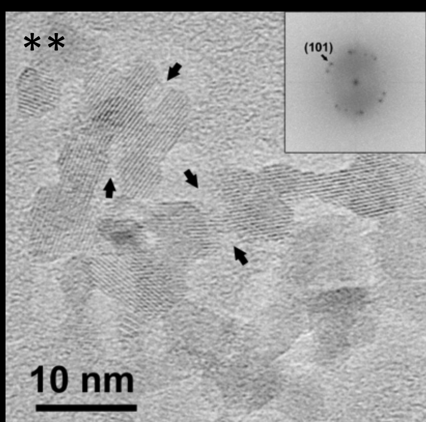
higher electron injection efficiency from LUMO of dye to the CB of TiO_2 due to the positive shifted flat band potential and fast electron transport rate resulting from reduced film resistance…***

**J. Photochem. Photobiol. A: Chem.* 2011, *219*, 180-187
**Energy 36 (2011) 1243-1254
*** Adv. Funct. Mater. 2010, 20, 509-515; Electrochim. Acta 2012, 77, 54-59; J. Alloys Comp. 2013, 548, 161-165

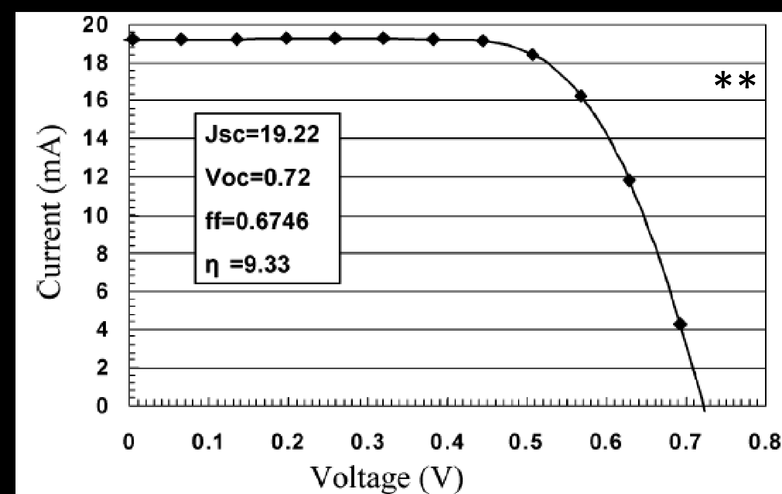


Lei et al. achieved 8.1% efficiency by using anatase *nc*-TiO_2 nanotube arrays on FTO substrate with relative high SSA benefiting from relatively long nanotube length of 20.8 µm ***.

Adachi *et al.* ** reported 9.3% conversion efficiency for a DSSC that include single-crystal- like TiO_2 nanowire based photoanode



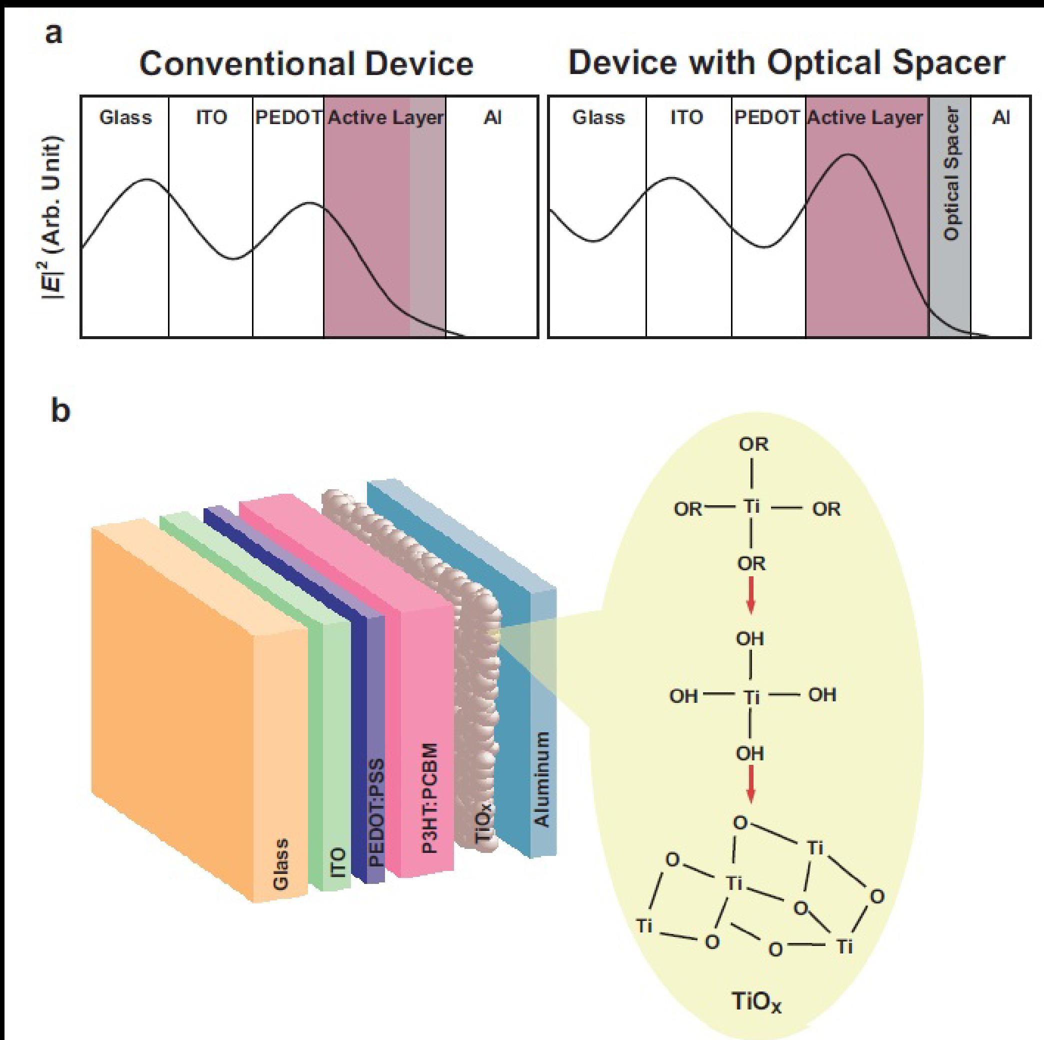
HRTEM image of several titania nanowires with single anatase structure formed by oriented attachment. Arrows in the HRTEM image indicate the indentations.

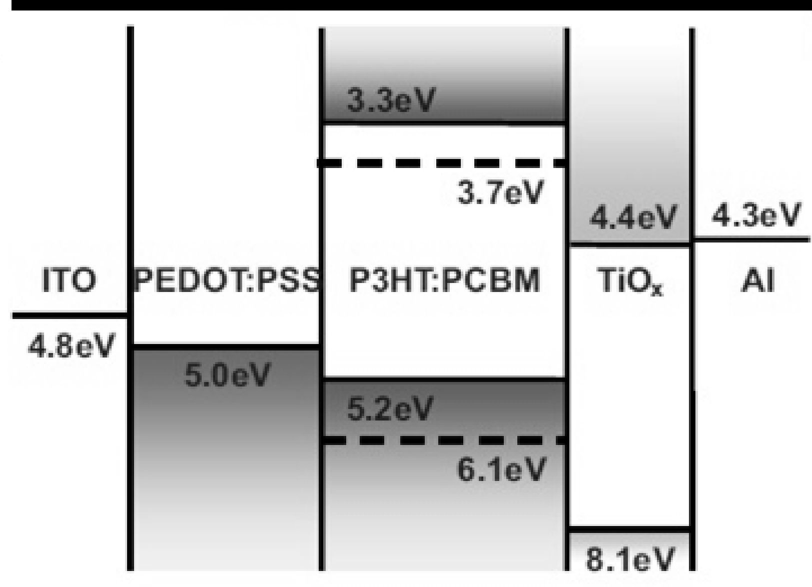


* *J.Photochem.Photobiol. C: Photochem. Rew.* 2012, *13*, 169- 189
** J. Am. Chem. Soc. 2004, 126, 14943-149949
*** J. Electrochem. Soc. 2003, 150, G488-493

TiO_2 in organic solar cells

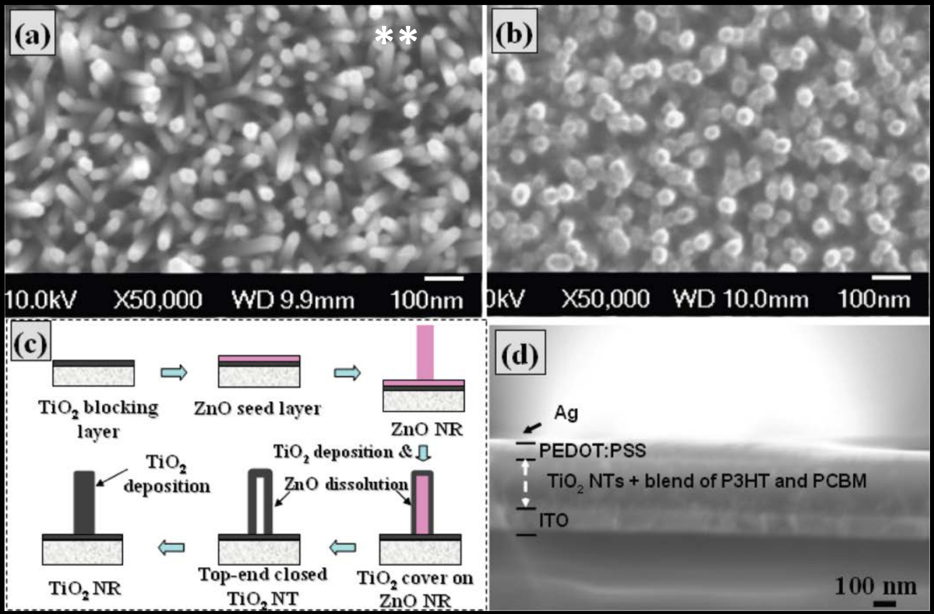
The CB energy level of TiO_2 provides its usage as an optical spacer, *i.e*. lower than the LUMO of most of the polymeric SCs and close to the Fermi energy level of metallic electrode. The addition of an optical spacer between the active layer and metal electrode increases the number of excitons formed



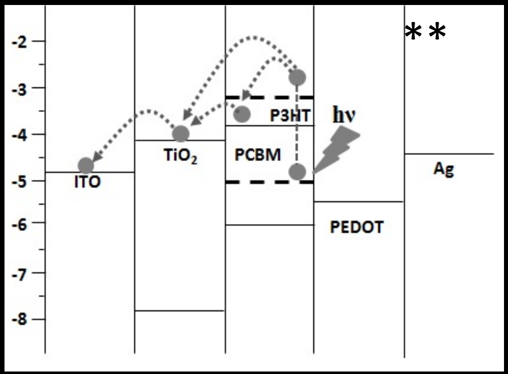


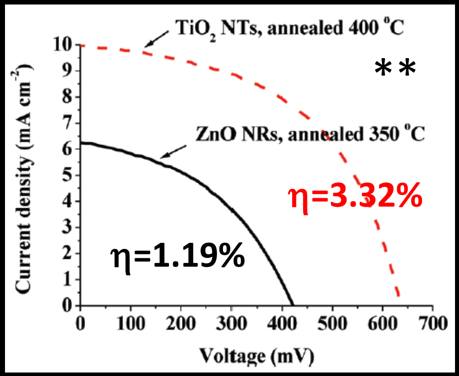
Adv. Mater. 2006, *18*, 572-576

The use of TiO_2 as an ETL in organic/inorganic hybrid OPV devices is more common *



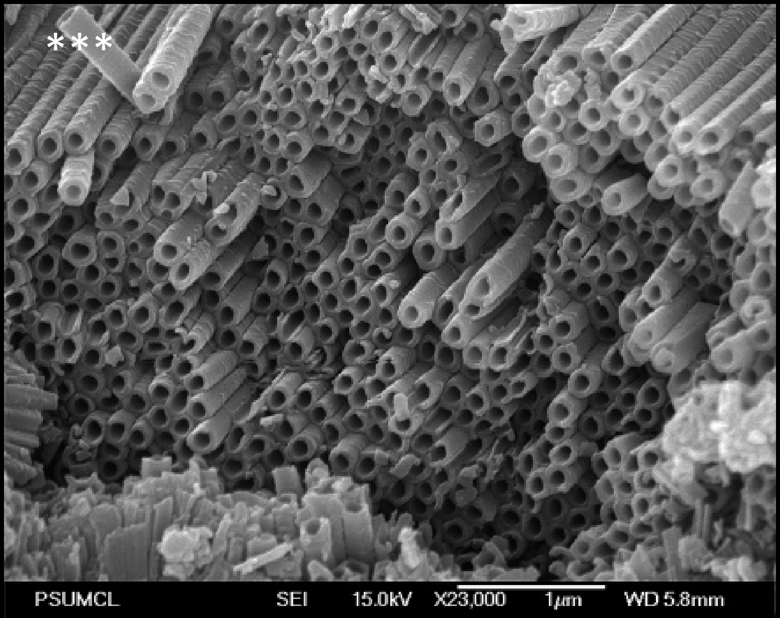
(a,b) The top view SEM images of ZnO nanorods and TiO_2 nanotubes, respectively, (c) the schematic process of preparing TiO_2 nanotubes, and (d) the cross section of hybrid solar cell photoelectrode using TiO_2 nanotubes.





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



FESEM image of a mechanically fractured 4 μm long TiO2 nanotube array sample.

*_Sol. Energy Mater. Sol. Cells_ 2008, _92_, 1445-1449

*** Langmuir 2007, 23, 12445-12449

**J. Phys. Chem. C 2010, 114, 21851–21855

Why?

How?

What?

- *Prog. in Photovol.: Res. and Appl.* 2012, 20, 698-710
- *Solar En. Mater. Solar Cells* 2012, 102, 109-113
- *Solar En. Mater. Solar Cells* 2012, 98, 417-423
- *J. Photochem. Photobiol. A: Chem.* 2004, 164, 203–207
- *Solar En. Mater. Solar Cells* 2009, 93, 820–824
- *Renew. Sust. En. Rev.* 2011, 15, 3717–3732

Elias Stathatos

Çiğdem Şahin

Gamze Saygılı

Thanks For Your Attention