

# Advances in nanostructuring of titania thin films for dye-sensitized and hybrid photovoltaics

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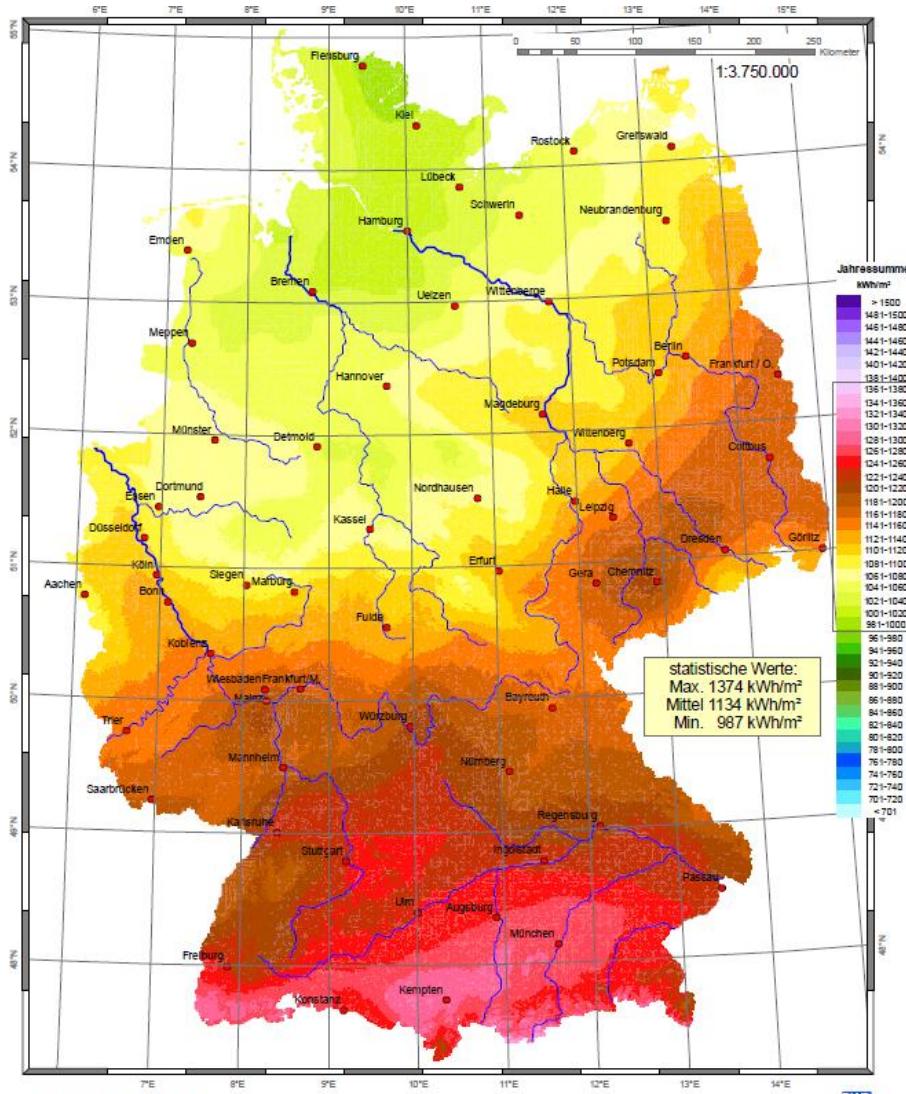


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<sup>3</sup>HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany





- solar energy available in Germany
- current technology mostly silicon (Si) based

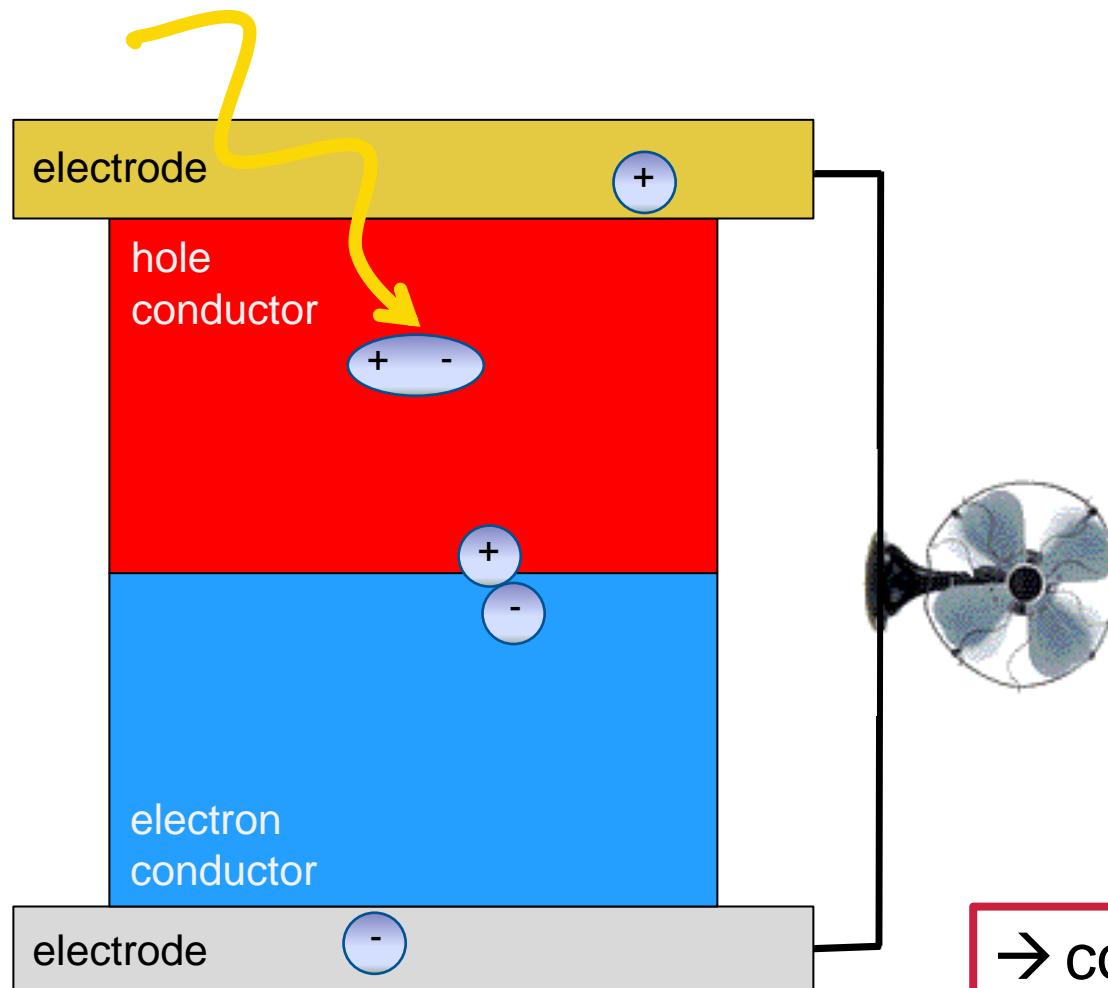


Wildpoldsried.de: Das Energiedorf

yearly sum of global horizontal irradiation (direct and diffuse radiation) in Germany, in the year 2011

measured in kWh/m<sup>2</sup>

max: 1374 kWh/m<sup>2</sup>  
mean: 1134 kWh/m<sup>2</sup>  
min: 987 kWh/m<sup>2</sup>



1. light absorption
2. exciton creation
3. exciton diffusion
4. charge separation, transport and extraction
5. charge recombination via external load

→ conversion of solar energy into electricity

thickness and type of active layer → amount of required material

conventional Si  
min. 150 µm;

„thin film“,  
amorphous Si  
10 µm



→ recyclability  
→ toxicity  
→ weight

thin film  
technologies  
1-2 µm



examples:

- CdTe  
(Cadmium Telluride)
- CIGS (Copper Indium Gallium Selenide)

novel technologies  
 $< 0.5 \mu\text{m} = 500 \text{ nm}$

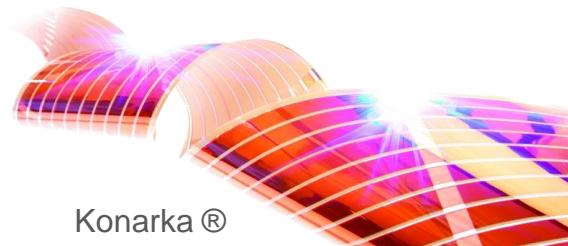


examples:

- organic solar cells
- hybrid (inorganic-organic) solar cells
- dye-sensitized solar cells

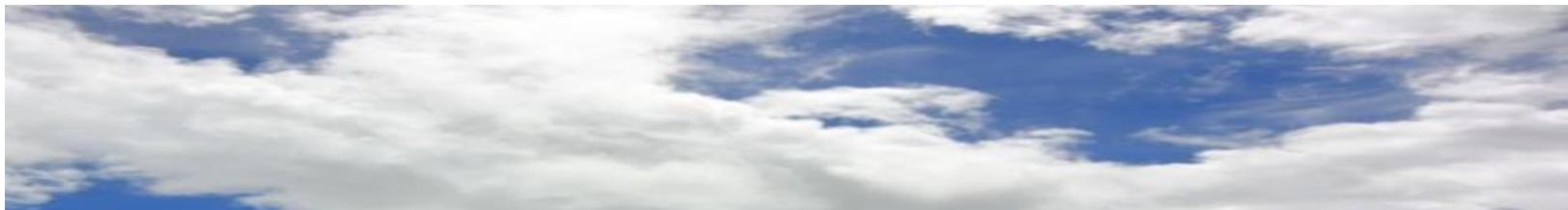
further important aspects of novel technologies:

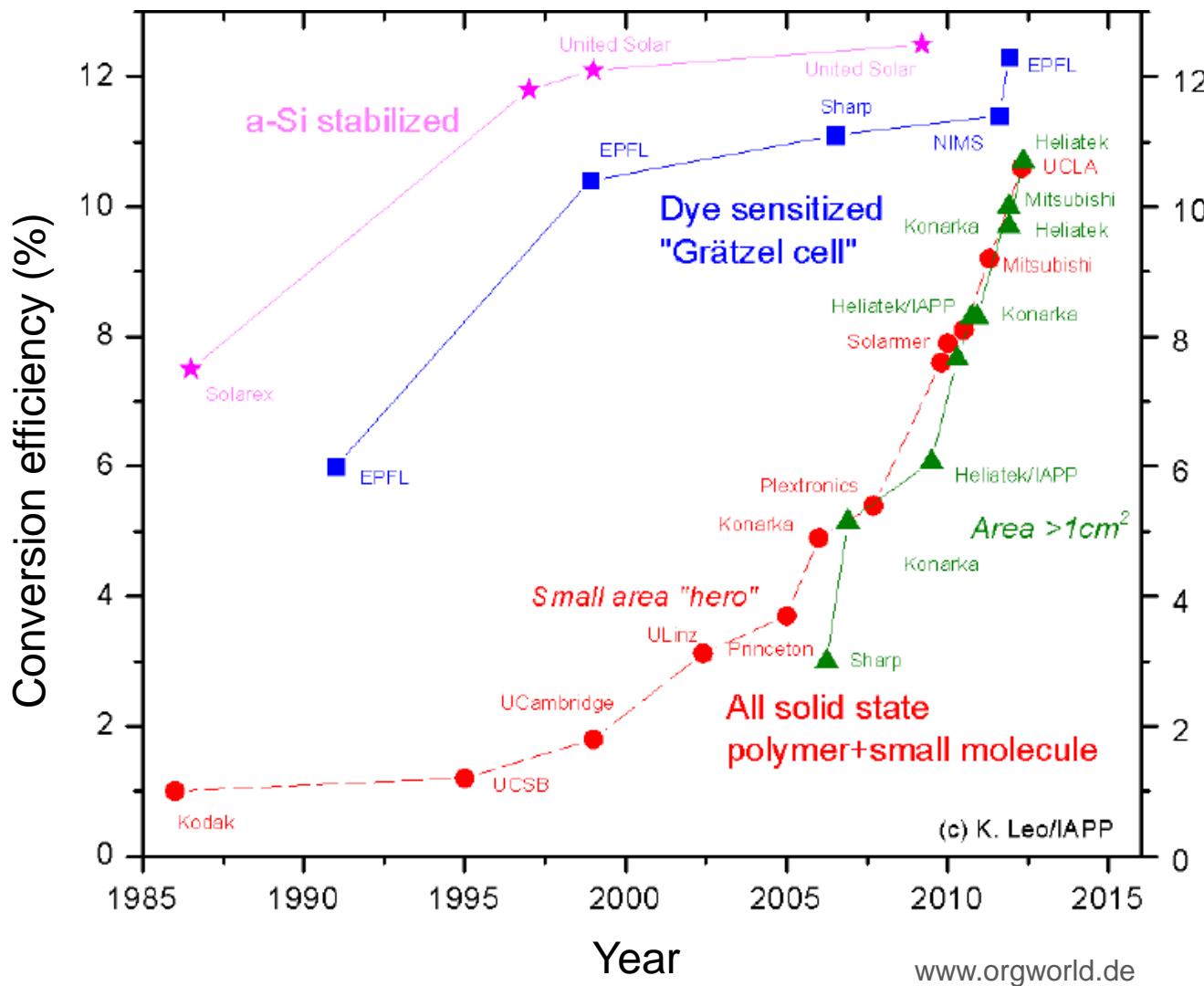
- no need for expensive production  
(clean room, high temperatures)
- mechanical flexibility  
→ roll-to-roll printing



phys.org: Si solar cell manufacturing centre of Trina Solar in Changzhou, China

- performance under cloudy conditions and at operation temperatures better than silicon





- promising trend of efficiencies
- soon exceeding amorphous silicon to be expected

**> 10 %  
in 2012**



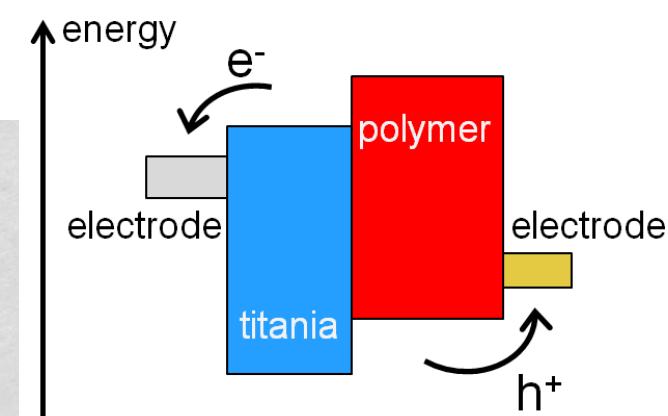
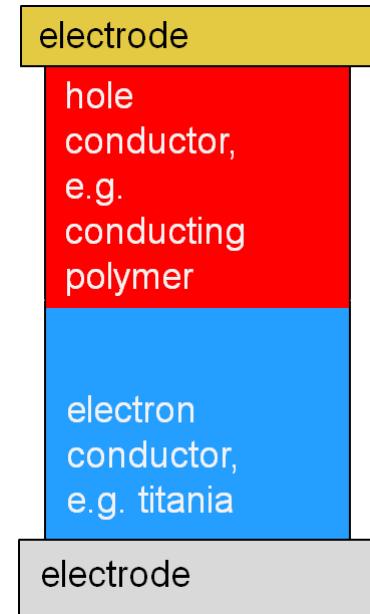
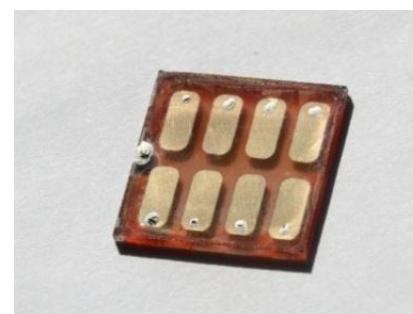
konarka.com

- **hybrid solar cells:**  
combination of inorganic material  
and organic material

- inorganic (titania)
- organic (polymers = plastics)

- cheap and easy to manufacture
- flexible
- thin films, little amount of material
- good at operation temperatures

- efficiencies: max. 4 %  
K. Kreis et al., Solar Energy Materials & Solar Cells 2002, 73, 51.

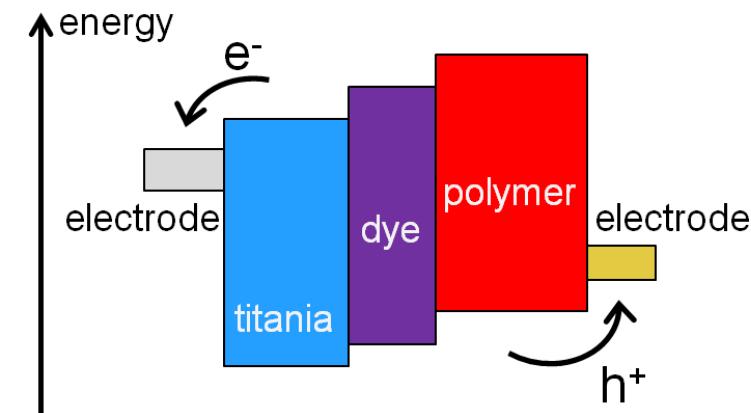
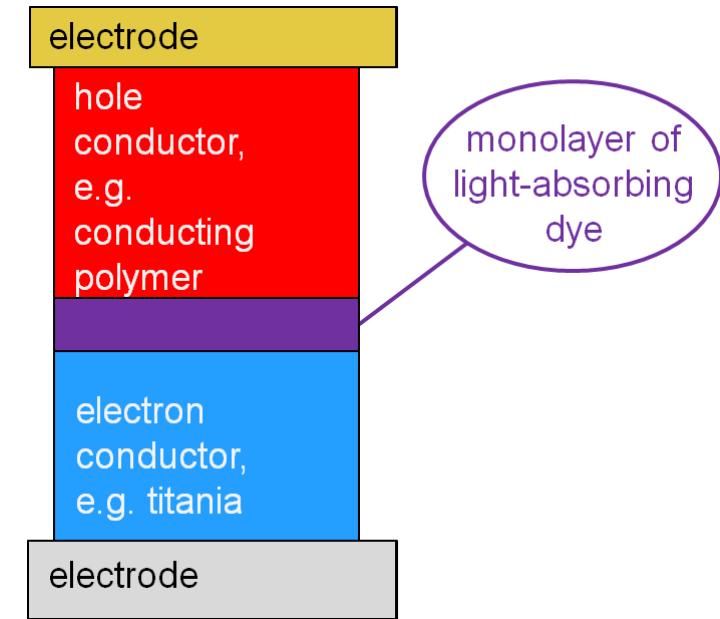
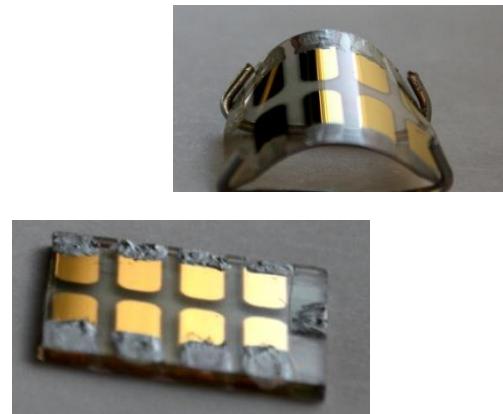


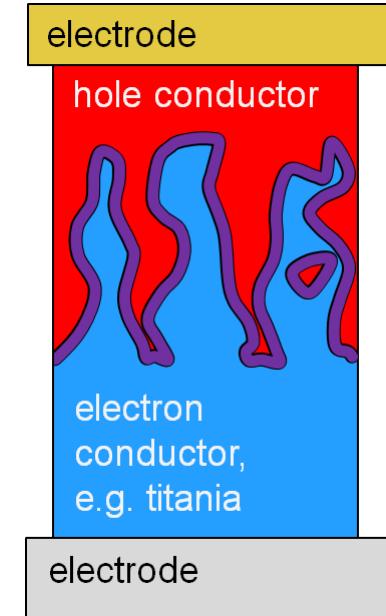
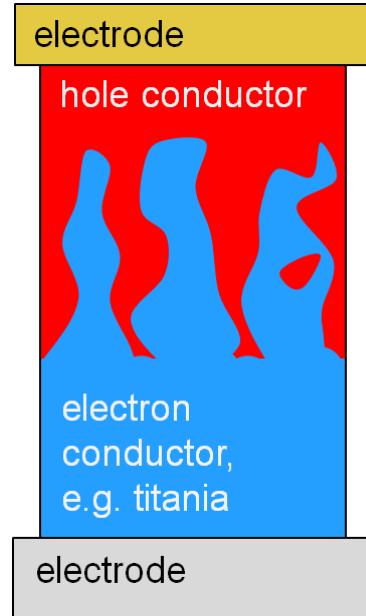
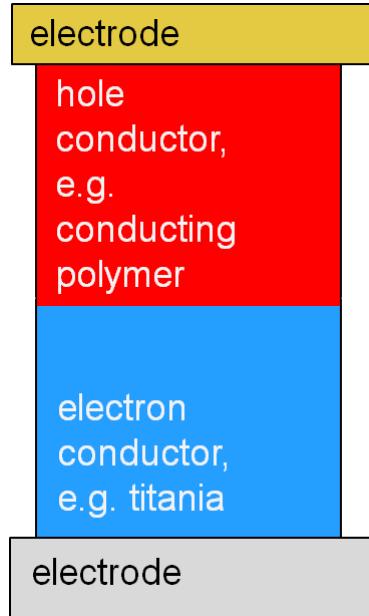
- **dye-sensitized solar cells:**  
additional light-absorbing dye layer  
between organic and inorganic material
- with liquid electrolyte as hole-conductor:  
efficiency max. 12.3 %
- with solid hole-conductor:  
efficiency max. 5 - 7.1 %

M. A. Green, et al., Prog. Photovolt.: Res. Appl. 2012, 20, 12-20; B. E. Hardin et al., Nature Photonics 2012, 6, 162-169



Fraunhofer ISE





bilayer structure:

- small interfacial area
- low efficiency of solar cells

nanostructures:

- larger interfacial area
- better charge separation
- more efficient solar cells

nanostructures with **dye**:

- larger interfacial area
- higher absorption
- more efficient solar cells

**Titania:**

- „Queen of fairies“ in Shakespeare's midsummer night's dream

*painting by  
Henry Fuseli,  
1796*

- largest moon  
of Uranus



titania = titanium dioxide,  $\text{TiO}_2$

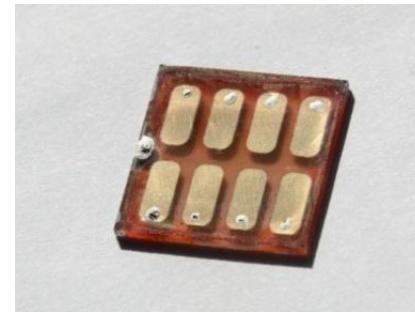
- ✓ cheap
- ✓ readily available
- ✓ non-toxic, biocompatible

common applications:

- pigment: titanium white
- food coloring: E171
- cosmetics: toothpaste, sunscreen

as semiconductor:

- solar cell
- photocatalyst
- gas sensor
- electrode material



<sup>1</sup>[fddb.info](http://fddb.info)

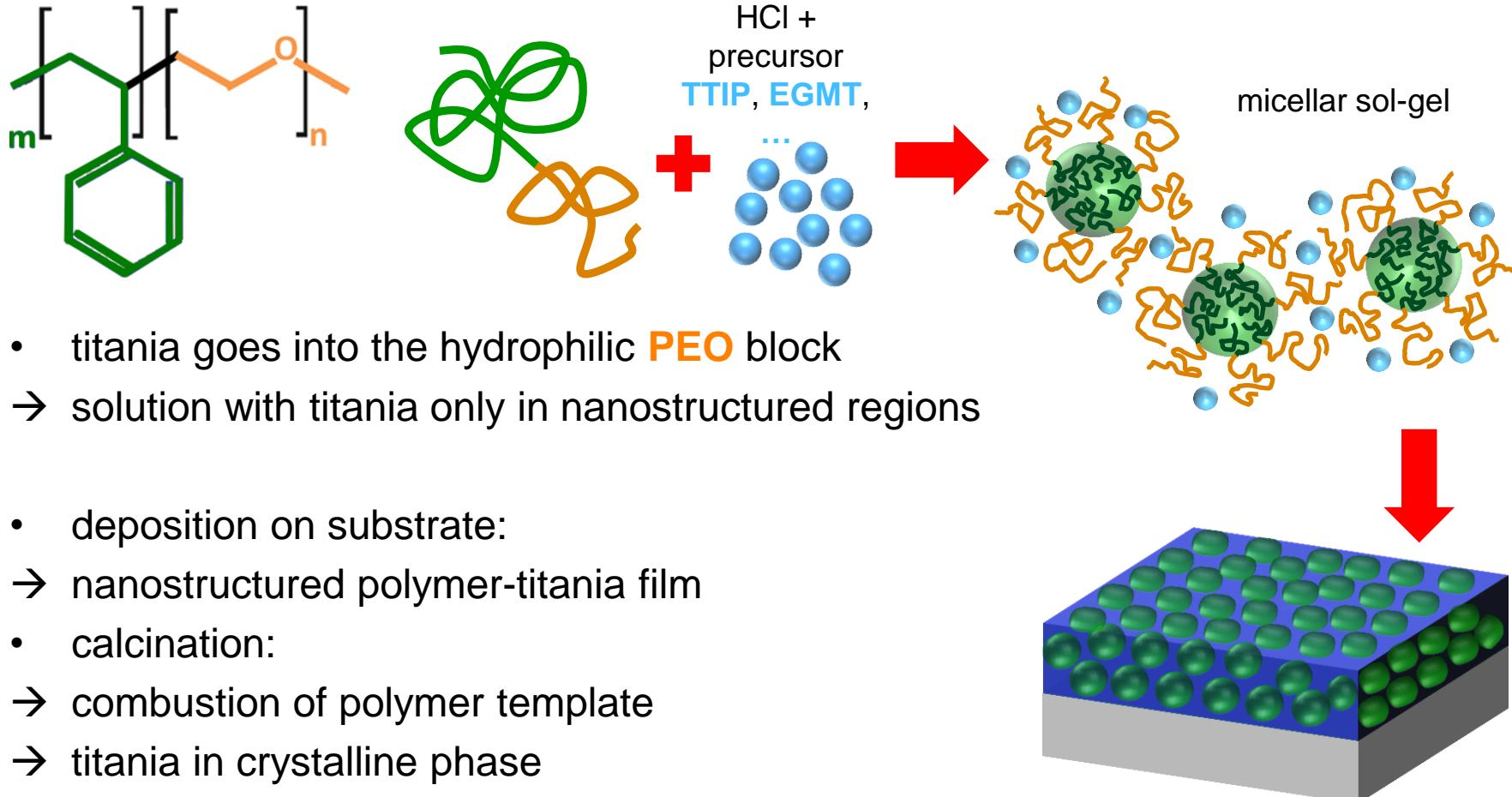
<sup>2</sup>[www.toptenz.net](http://www.toptenz.net)

<sup>3</sup>[www.profil-marketing.com](http://www.profil-marketing.com)

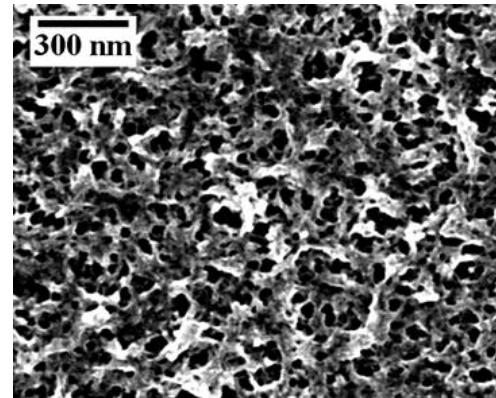
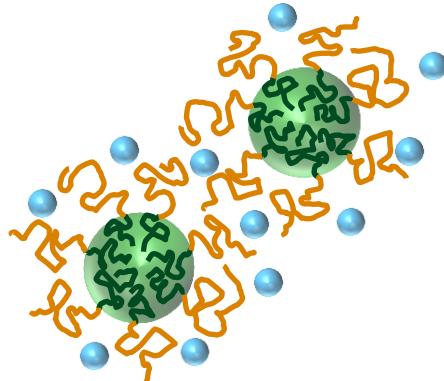
<sup>4</sup>[www.rxbright.com](http://www.rxbright.com)

<sup>5</sup>[www.treatment-skincare.com](http://www.treatment-skincare.com)

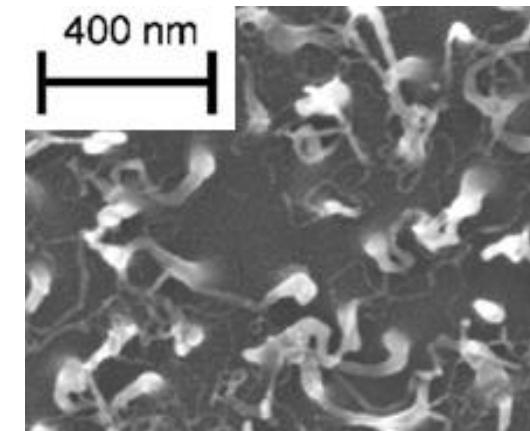
- usage of **block copolymer** template in synthesis of titania:  
block copolymer can be imagined like a two-colored spaghetti, e.g. **PS-block-PEO**  
chemically bond hydrophobic (e.g. **PS**) and hydrophilic polymer (e.g. **PEO**)



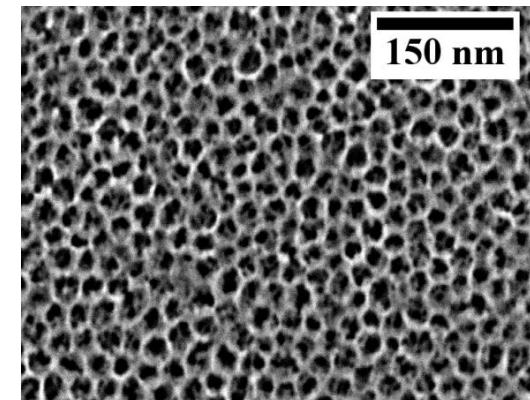
- titania from precursor **TTIP** with **PS-*b*-PEO** as template: worm-like nanostructures
- titania from precursor **TTIP** with **PDMS-*b*-PEO** as template: foam nanostructures
- titania from precursor **EGMT** with **PS-*b*-PEO** as template: crystalline titania at temperatures below 100 °C, nano-network



M. Rawolle et al., ChemPhysChem  
13 (2012), 2412.

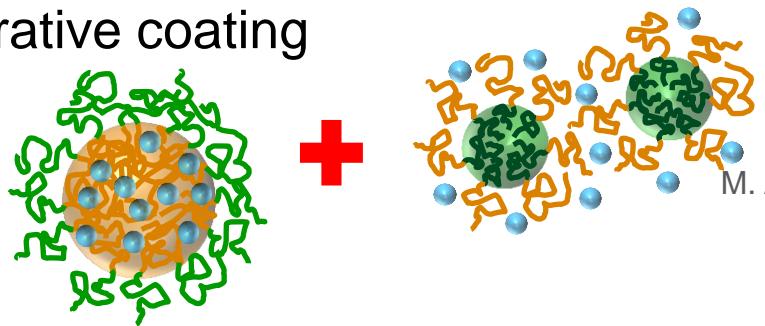


M. Rawolle et al., Chem. Soc. Rev.  
2012, DOI: 10.1039/c2cs15321

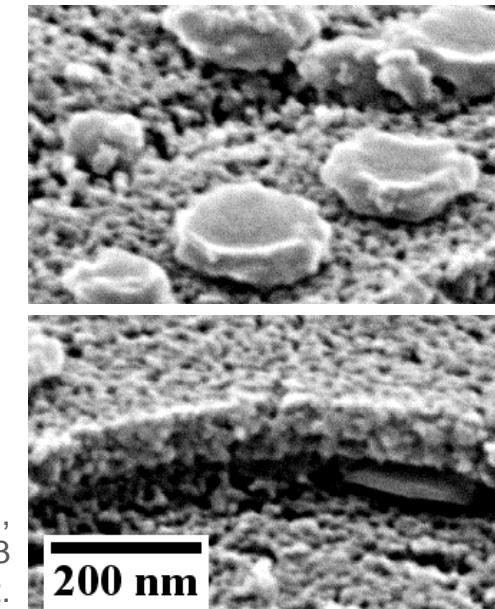


M. Rawolle et al., Small 7 (2011),  
884.

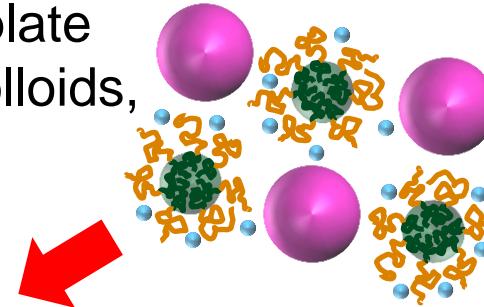
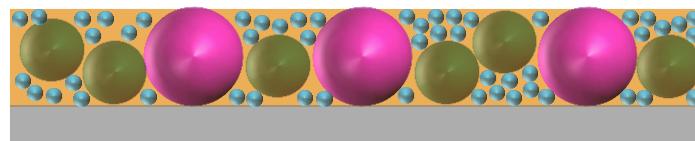
- combination of different sol-gel structures:
  - titania sponge and titania granules from precursor **TTIP** with polymer template **PS-*b*-PEO** (different weight fractions)
  - iterative coating



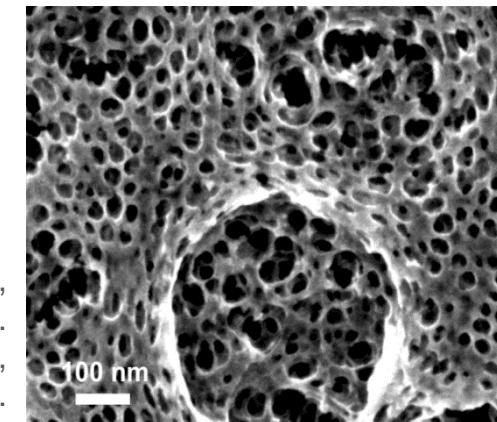
M. A. Niedermeier et al.,  
Nanotechnology 23  
(2012), 145602.



- combination of polymer template **PDMS-*b*-PEO** with **PDMS** colloids, titania from precursor **TTIP**



G. Kaune et al.,  
ACS Appl. Mater.  
Interf. 1 (2009),  
2862.



- research on solar cells necessary

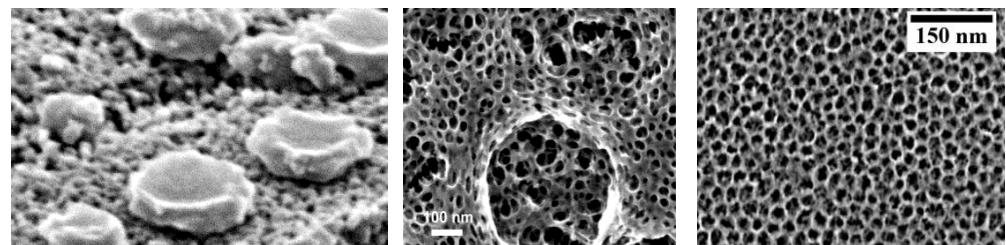
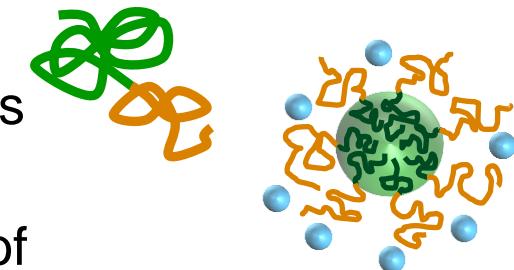


- interesting novel technologies:
  - hybrid solar cells
  - dye-sensitized solar cells



- nanostructuring of inorganic semiconductor material (e.g. titania) necessary:

- combination of block copolymers as templates with sol-gel chemistry
- towards hierarchical structures with addition of iterative coating or colloids in sol-gel



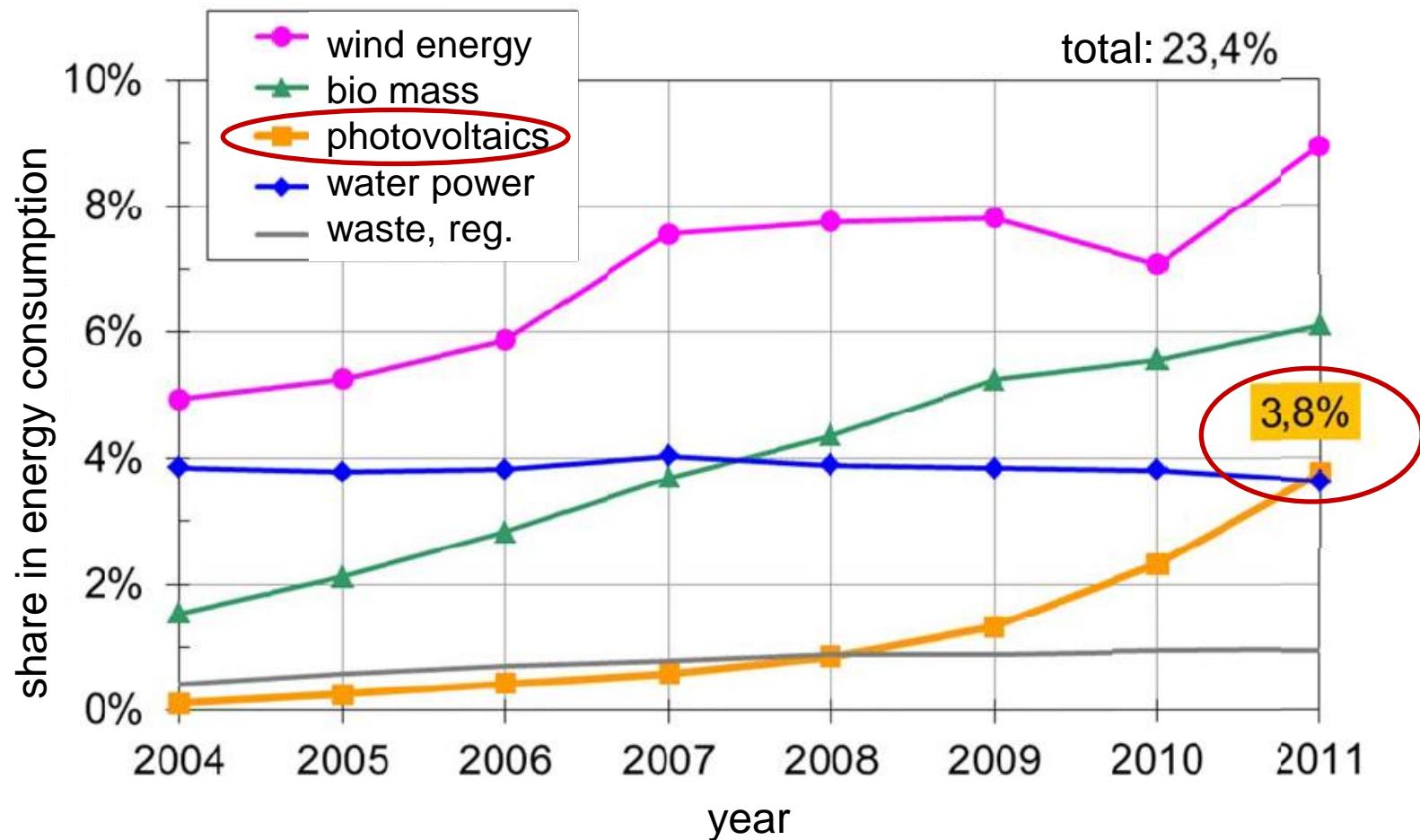
- all the members of the Chair for Functional Materials, Physik-Department, TUM
- funding:  
DFG SPP 1181  
“Nanomat”  
(MU1487/2,  
HU1427/1 and  
GU771/2)





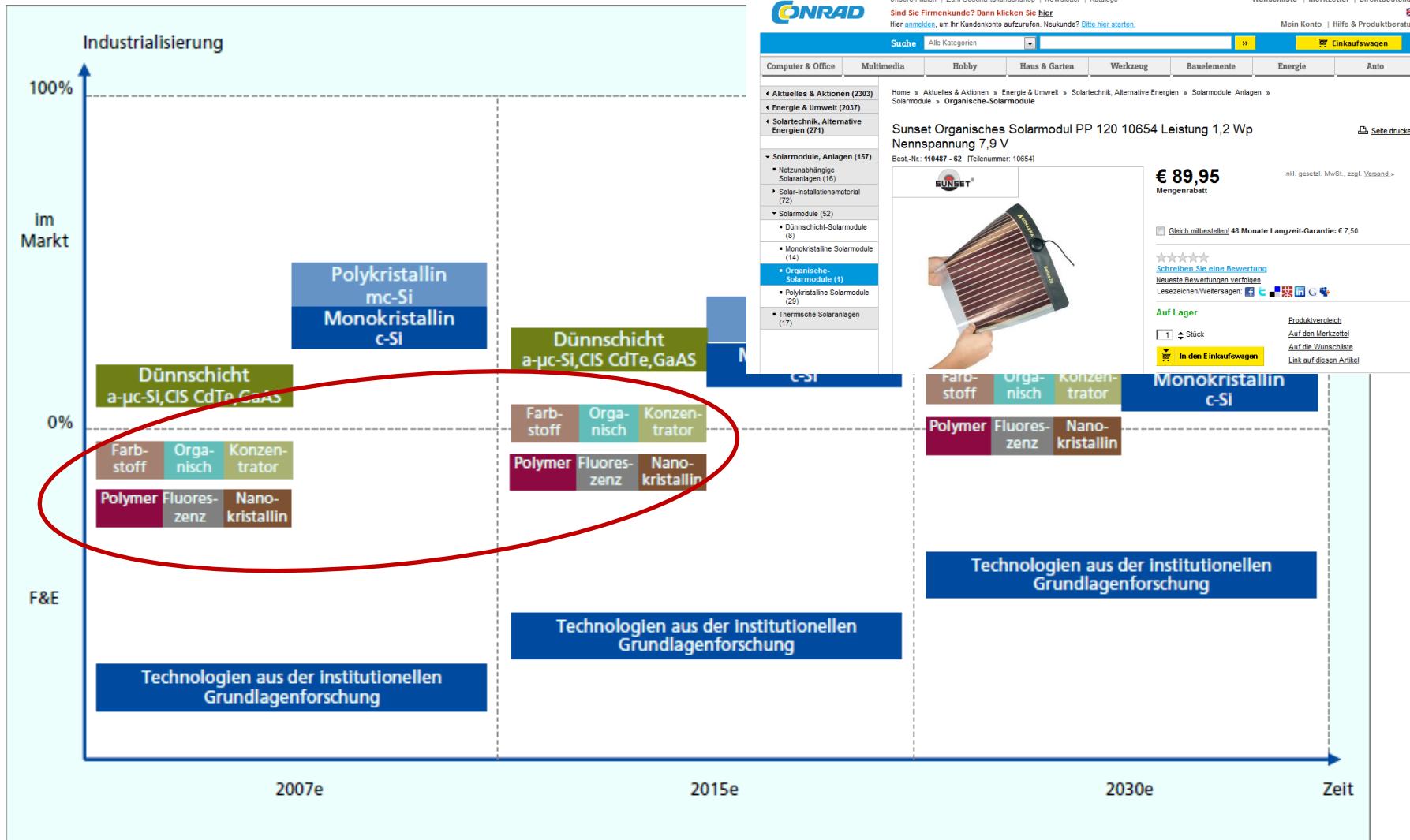
- motivation: solar cells and the need for research
- basic principle of a solar cell
- different types of „novel“ solar cells
  - the need for nanostructures
    - hybrid solar cells
    - dye-sensitized solar cells
- ways to tackle the synthesis of nanostructured materials
  - titania as electron acceptor
  - synthesis with block copolymer templates
  - towards hierarchical structures
- summary

## installed PV power in Germany

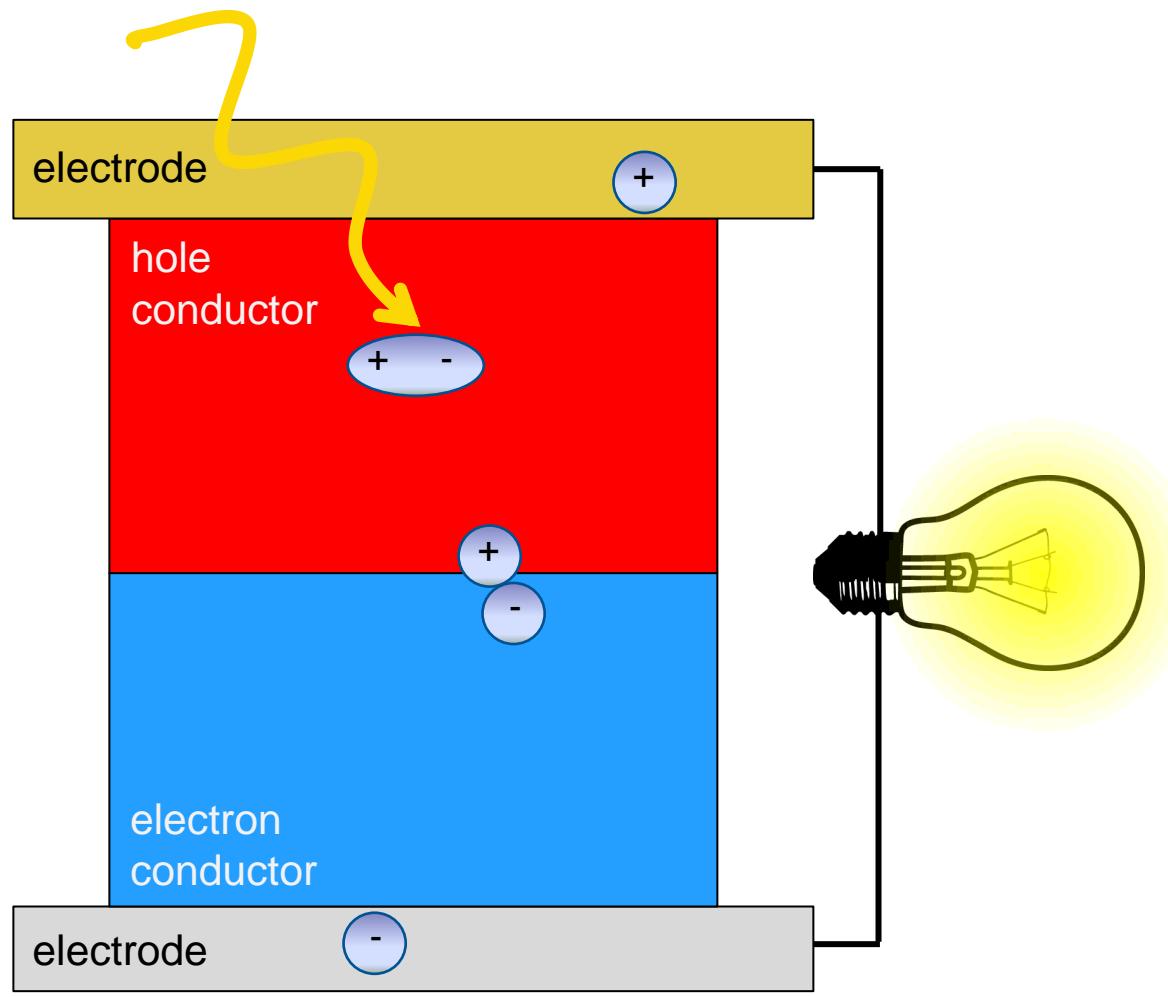


→ huge growth potential

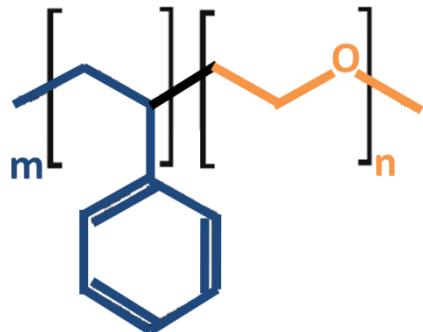
Aktuelle Fakten zur Photovoltaik  
in Deutschland, Dr. H. Wirth,  
Fraunhofer ISE, Freiburg,  
30.4.2012



Standortgutachten Photovoltaik in Deutschland, EuPD Research + ifo Institut München, 2008

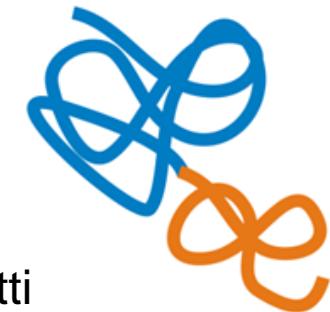


- polymer template for the creation of nanostructures:  
block copolymer, e.g. **PS-block-PEO**



two polymers with different chemical and physically properties – chemically bond

can be imagined like a two-colored spaghetti



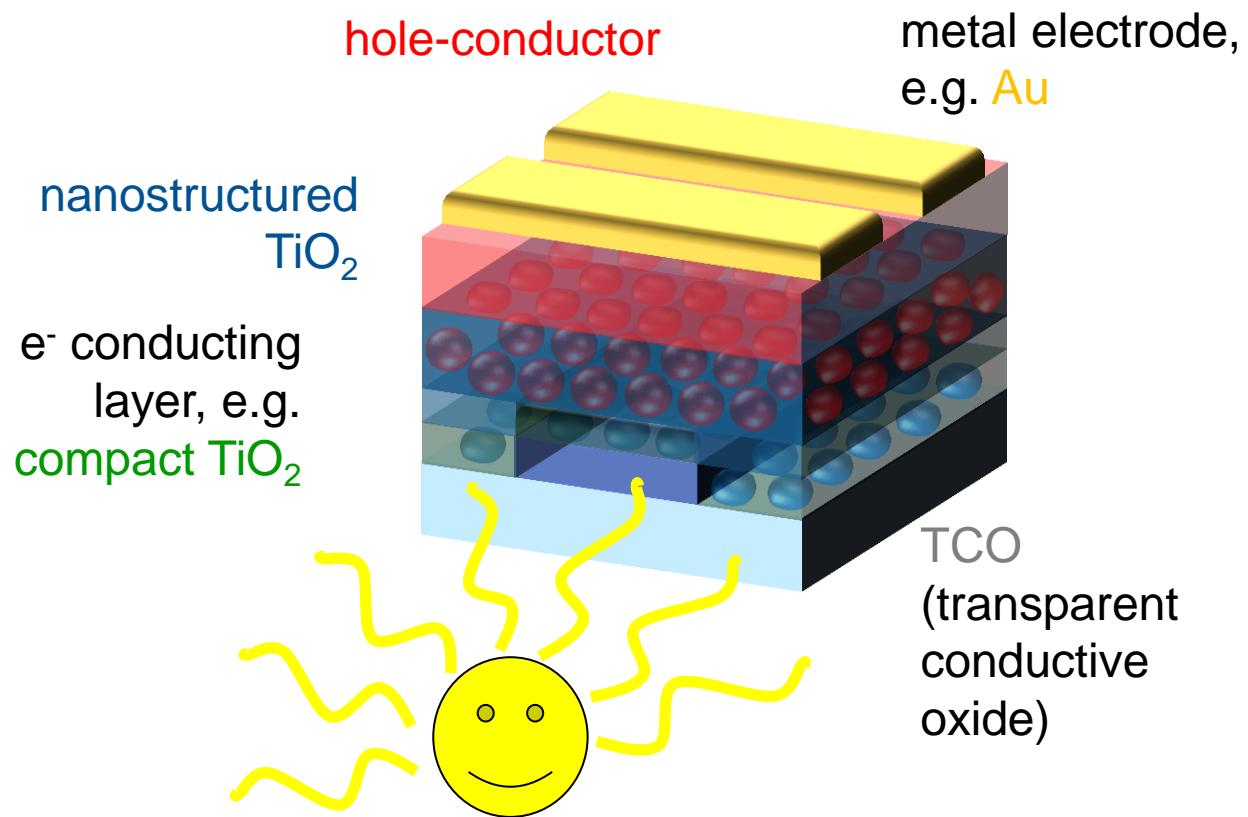
- amphiphilic block copolymer:  
one hydrophobic block (e.g. **PS**) and one hydrophilic block (e.g. **PEO**)  
→ microphase separation



increasing volume fraction of blue part (in example **PS** block)

G. Strobl, The Physics of Polymers, Springer, 1997

## hybrid solar cell setup



## dye-sensitized solar cell setup

