Elektrochemische Abscheidung von nanoporösen Metalloxid-Filmen für farbstoffsensibilisierte Solarzellen

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Overview

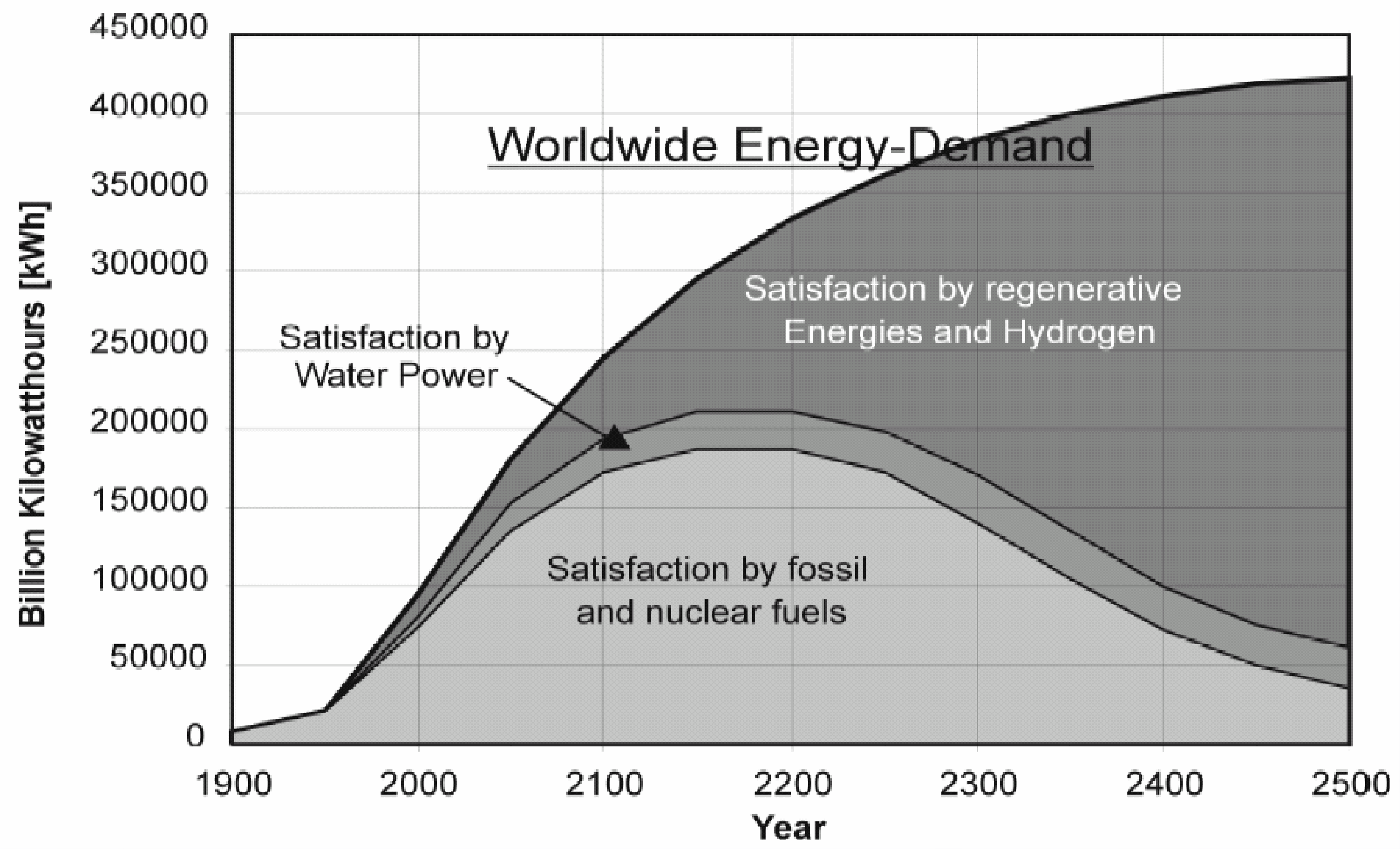
- **Introduction and Motivation**
    - Solar cells as possible solution for the energy problem
    - Dye-sensitized solar cells (DSSC)

- **Electrodeposition of nanoporous ZnO films for DSSC** using
    - Organic molecules (e.g. dye molecules)
    - Surfactants

- **Photoelectrochemical properties of electrodeposited ZnO**
    - Electron transport properties

- **Electrodeposition of TiO_2**

The energy problem



Solar energy as possible solution ?

Current energy consume per year: 1.4×10^{14} kWh
Sun Power: $P_{Sun} = 4 \times 10^{26}$ W
Sun power that reaches Earth: $P_{Earth} = 1.8 \times 10^{17}$ W → 1.6×10^{18} kWh power year
About 10000 times the energy consume !!

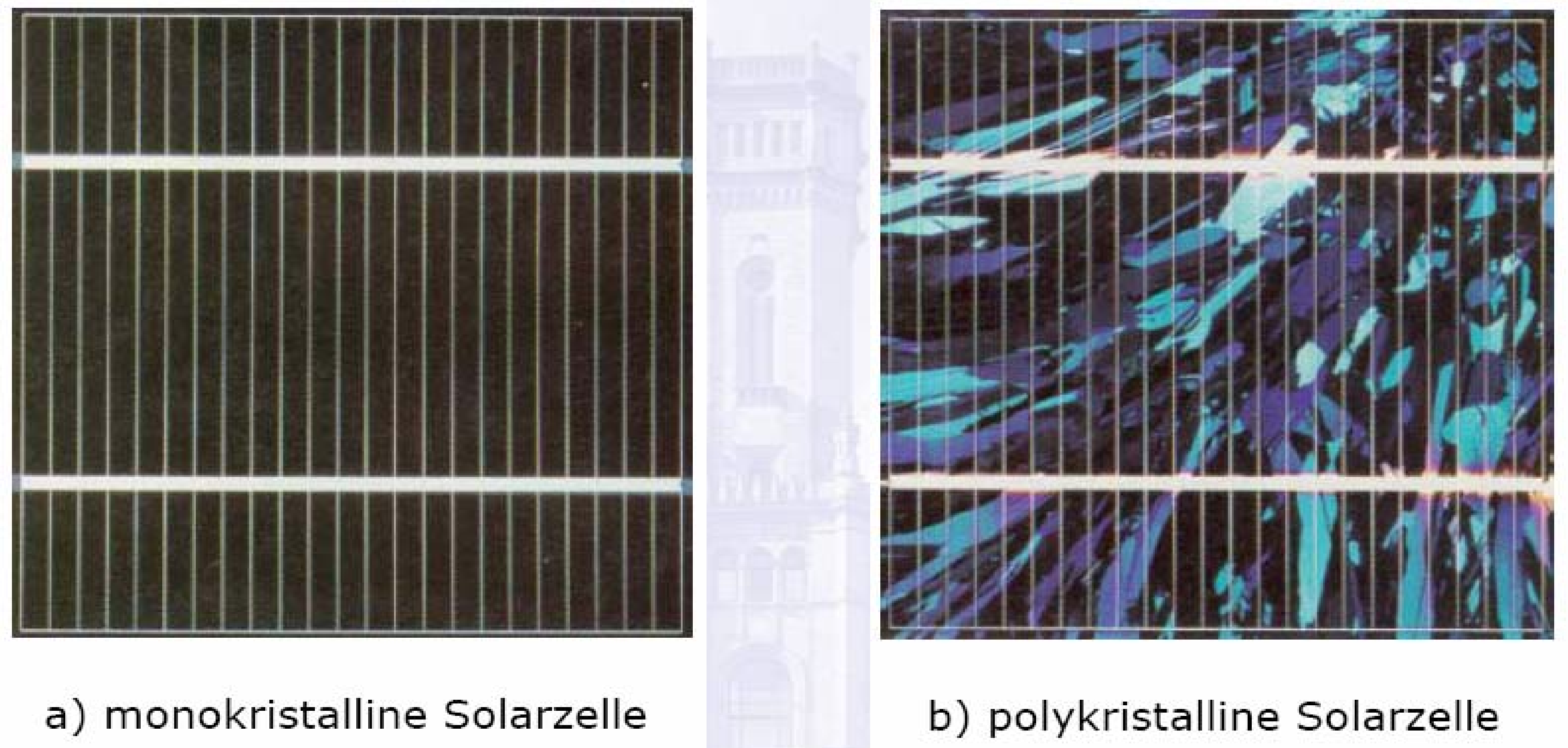
How can it be used ?
Assume:
- 8 h light per day , 1 kW/m^2 (Solar constant: 1.4 kW/m^2)
- Efficiency: 10 % (typical value for commercial solar cells)

→ Area of 700 km x 700 km needed (e.g. = 1/5 of the Sahara desert)

Loss of Energy (e.g. 30 % for 3000 km Sahara desert – Central Europe)
→ Area of 850 km x 850 km (1/4 of the Sahara desert)

In principle, it is possible to satisfy the whole energy demand solely by solar energy, based on current technology !

The „classical“ silicon solar cell



a) monokristalline Solarzelle

b) polykristalline Solarzelle

Si solar cells are expensive / consume much energy for production !

- need to have very pure silicon

- many production steps

→ Electric energy from Si solar cells is still much more expensive than from fossil or nuclear fuels

Efficiency of solar cells

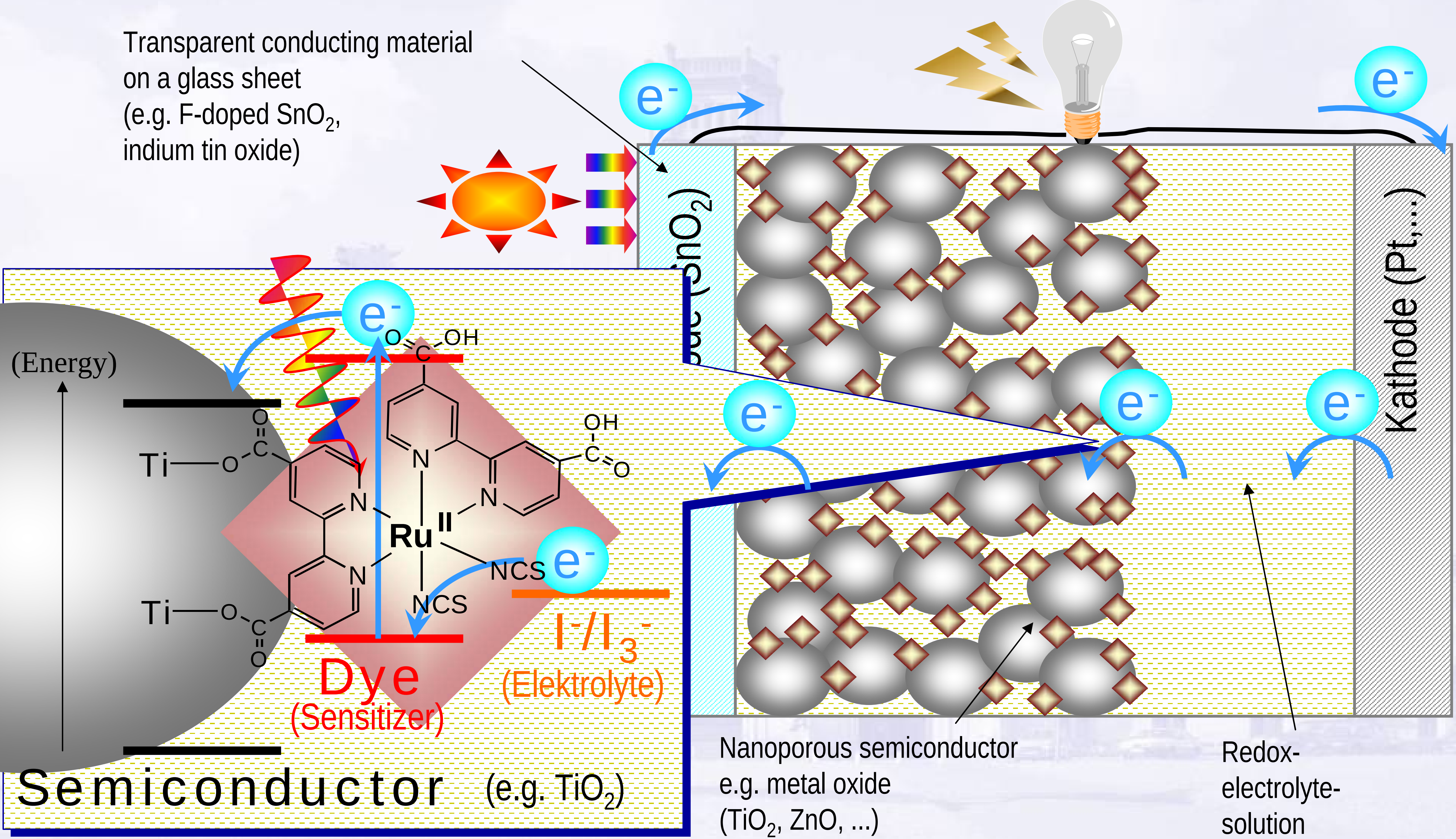
Type of cell	**Efficiency**	
	laboratory *(2005)*	commercial production *(2003)*
Silicon (monocrystalline)	25 %	17 %
Silicon (polycrystalline)	20 %	14 %
GaAs (monocrystalline)	25 %	
GaAs (polycrystalline)	18 %	
InP (monocrystalline)	22 %	

High efficiency, but toxic materials ......

Alternative cells: Less efficient, but much ch

Silicon (amorphous)	9.5 %	
Thin Film Solar Cells, e.g.:		
Copper indium gallium selenide (CIGS)	18.4 %	11 %
CdTe	16.5 %	10.7 %
Dye-sensitized solar cells	11.5 %	7-8 %
Organic semiconductors	3-4 %	

Dye-sensitized solar cells (DSSC)



Transparent conducting material on a glass sheet (e.g. F-doped SnO_2, indium tin oxide)

Nanoporous semiconductor e.g. metal oxide (TiO_2, ZnO, ...)

Redox-electrolyte-solution

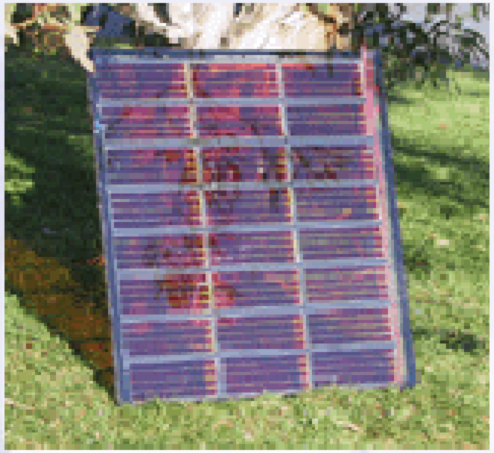
Semiconductor (e.g. TiO_2)

Dye-sensitized solar cells (DSSC)

Prototype-Cells:

- Transparent !
- Colorful !

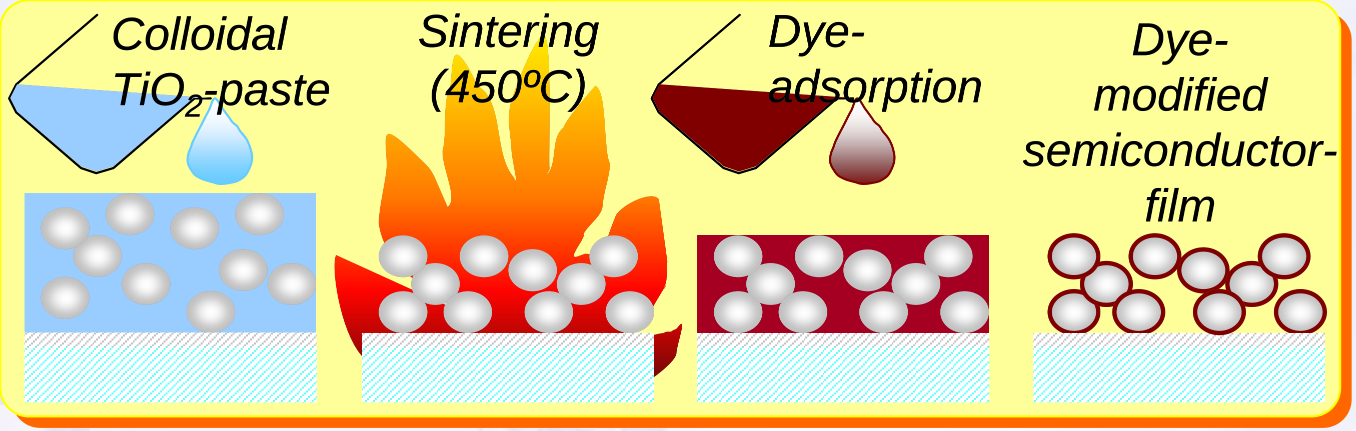
→ More applications !



Solar panels e.g. for house facades (Dyesol Ltd., Australia)

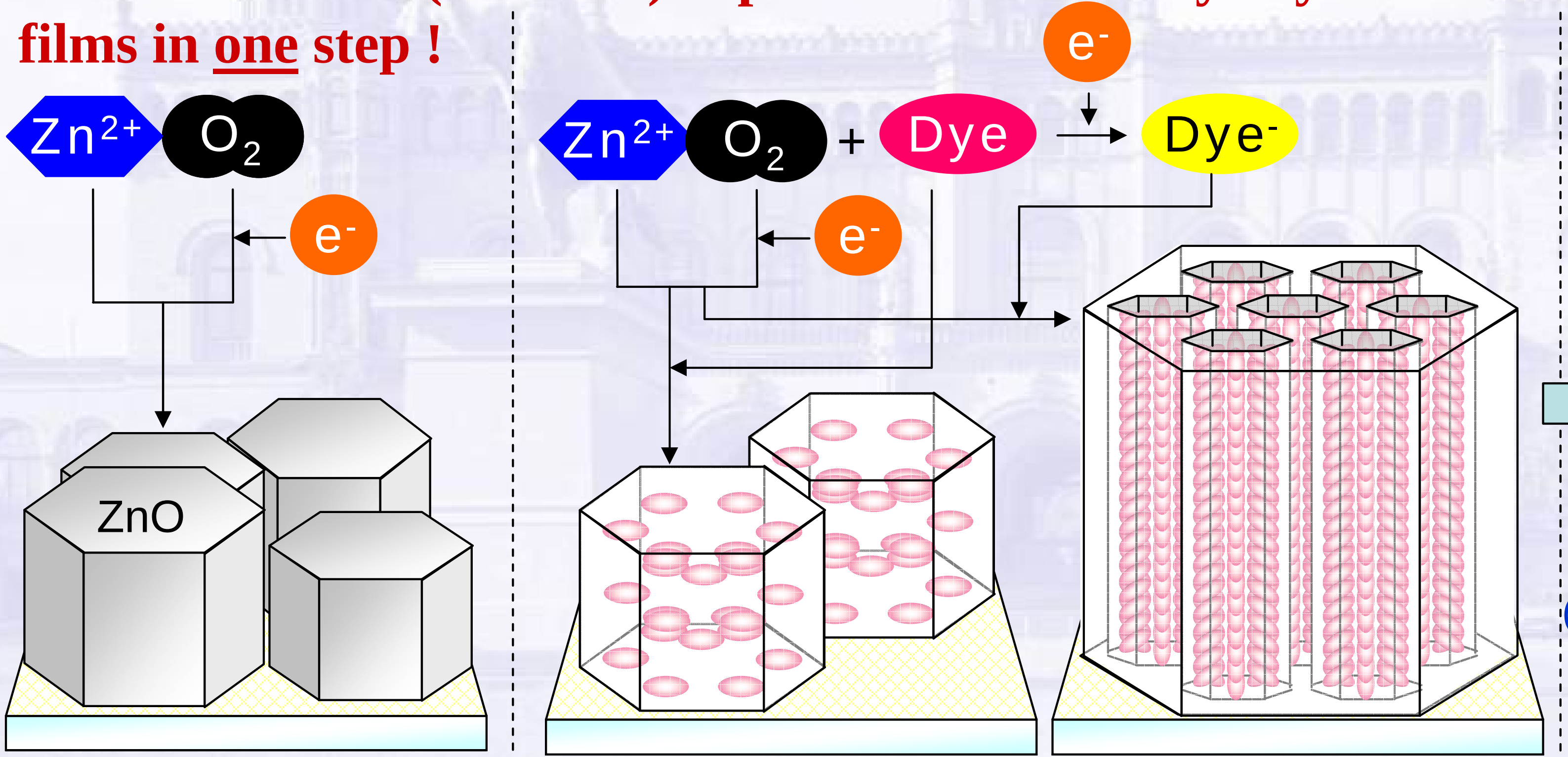
Preparation of metal oxide films for DSSC

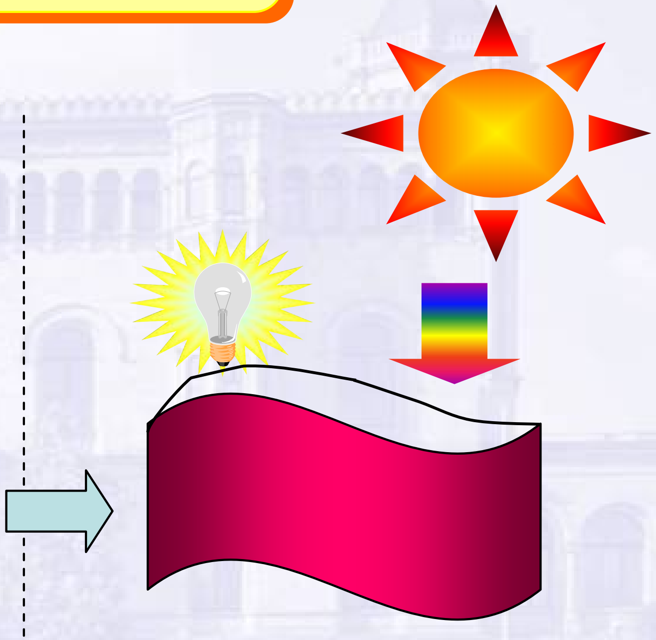
Conventional Method („Grätzel cell“):



NEW:

Electrochemical (cathodic) deposition of ZnO / dye hybrid films in <u>one</u> step !



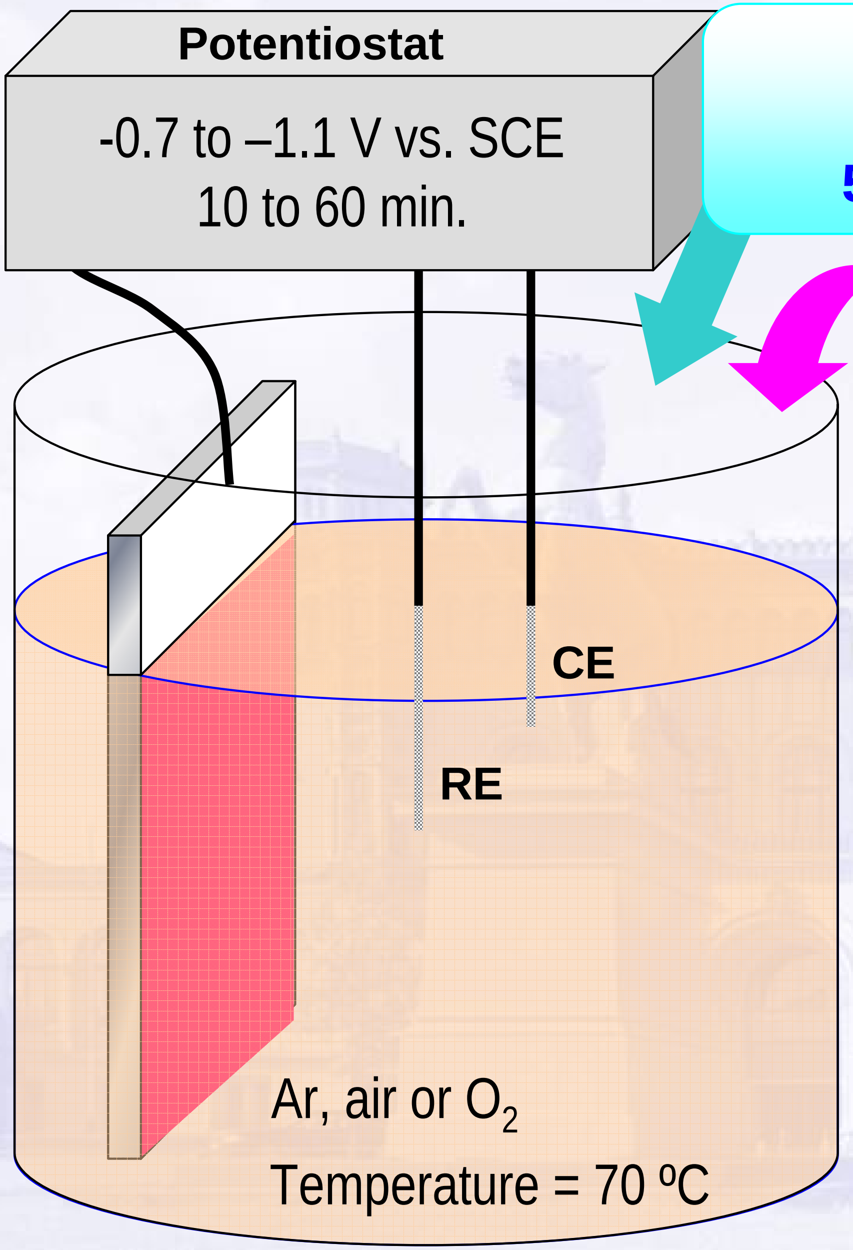


Flexible solar cells !

(no high temperature necessary)

T. Yoshida, K. Miyamoto, N. Hibi, T. Sugiura, H. Minoura, D. Schlettwein, T. Oekermann, G. Schneider, D. Wöhrle, *Chem. Lett.* **1989**, 599.

Electrodeposition of ZnO / dye films



Potentiostat

-0.7 to –1.1 V vs. SCE
10 to 60 min.

$0.1\ M\ Zn(NO_3)_2$
or
$5\ mM\ ZnCl_2 + 0.1\ M\ KCl$

$Zn^{2+} + NO_3^- + 2e^- \rightarrow \mathbf{ZnO} + NO_2^-$

$Zn^{2+} + 1/2\ O_2 + 2e^- \rightarrow \mathbf{ZnO}$

25 to 50 µM
Dye

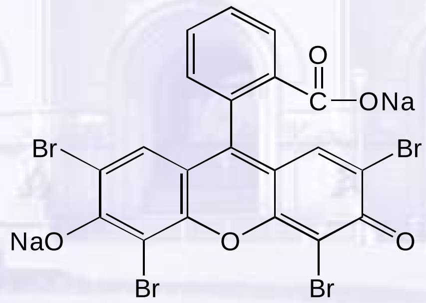
CE

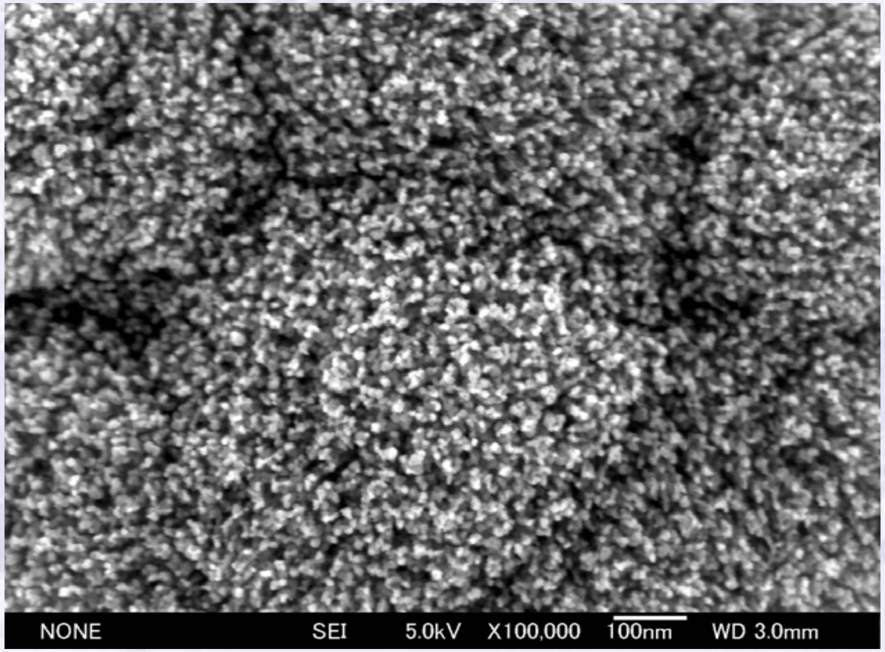
RE

Ar, air or O_2

Temperature = 70 ºC

Nano-porous ZnO / Eosin Y – film



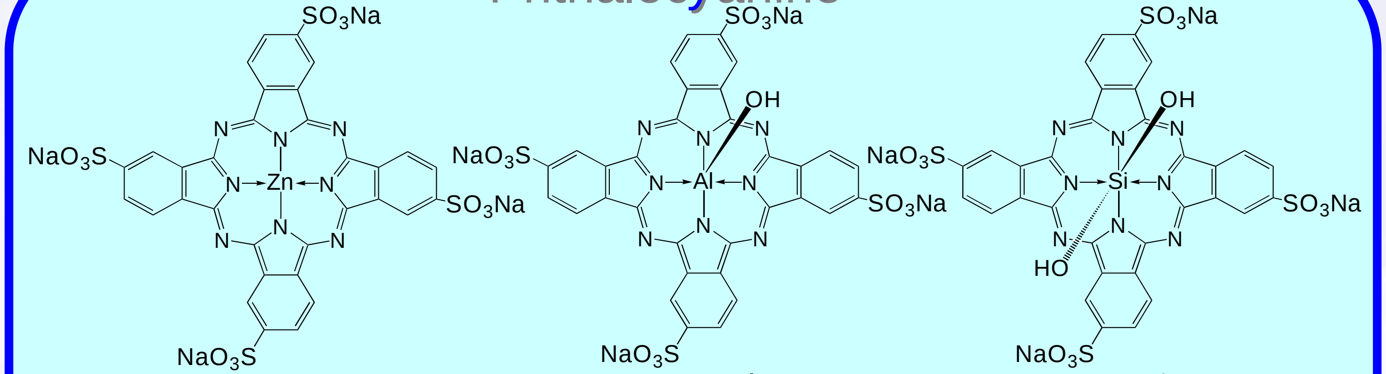


T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, *Adv. Mater.* **2000**, *12*, 1214.
T. Yoshida, T. Oekermann, et al., *Electrochemistry* **2002**, *70*, 470.
T. Yoshida, T. Pauporte, D. Lincot, T. Oekermann, H. Minoura, *J. Electrochem. Soc.* **2003**, *150*, C608.

Leibniz
Universität Hannover

Examples of used dye molecules

Phthalocyanine

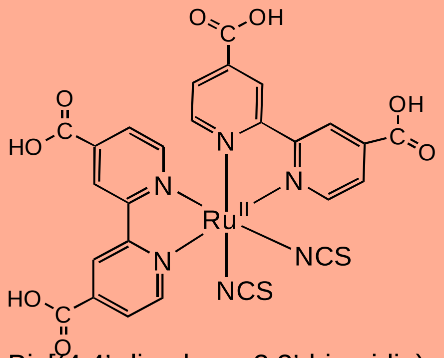


TSPcZn
Mw = 986.1
λmax = 680 nm (aq.)
ε = 155,800 M^{-1} cm^{-1}

TSPcAl
Mw = 964.7
λmax = 674 nm (aq.)
ε = 132,000 M^{-1} cm^{-1}

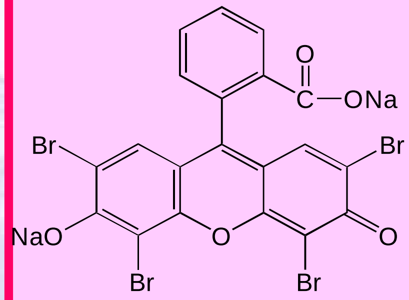
TSPcSi
Mw = 948.8
λmax = 676 nm (aq.)
ε = 91,100 M^{-1} cm^{-1}

Ru-Komplex



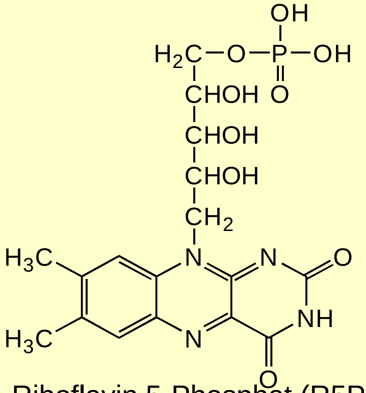
Bis[(4,4’-dicarboxy-2,2’-bipyridin)(thiocyanato)]Ru(II) (N3)
Mw = 705.6
λmax = 371, 500 nm (aq.)
ε = 11,800, 11,500 M^{-1} cm^{-1}

Eosin Y



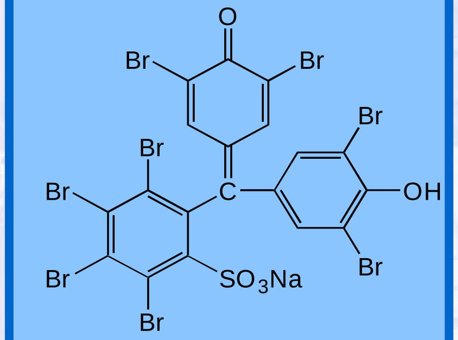
Eosin Y (EY)
Mw = 691.9
λmax = 514 nm (aq.)
ε = 91,600 M^{-1} cm^{-1}

Riboflavin



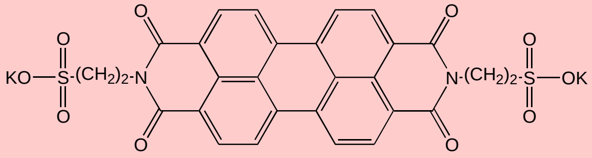
Riboflavin 5-Phosphat (R5P)
Mw = 527.3
λmax = 445 nm (aq.)
ε = 12,500 M^{-1} cm^{-1}

Phenolblau



Tetrabromophenolblau (TB)
Mw = 1007.6
λmax = 445 nm (aq.)
ε = 12,500 M^{-1} cm^{-1}

Perylene

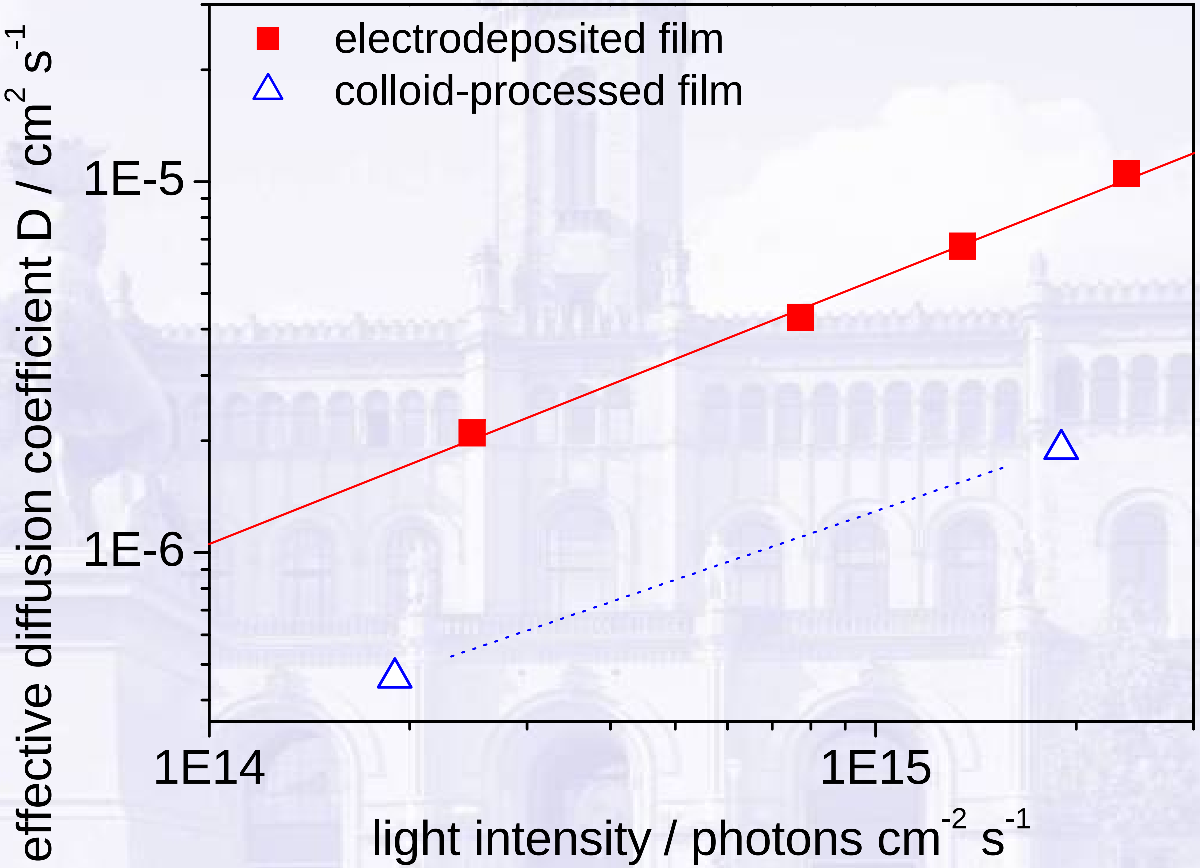


N,N’-Bis-(ethylensulfat)-3,4,9,10-perylentetracarbonsäurediimid (PTCDI)
Mw = 714.9
λmax = 500 nm (aq.)
ε = 16,500 M^{-1} cm^{-1}

Important:
Acid groups !

Effective electron diffusion coefficients D_n

From measurement of electron transport properties by IMPS / IMVS (Intensity Modulated Photocurrent / Voltage Spectroscopy):



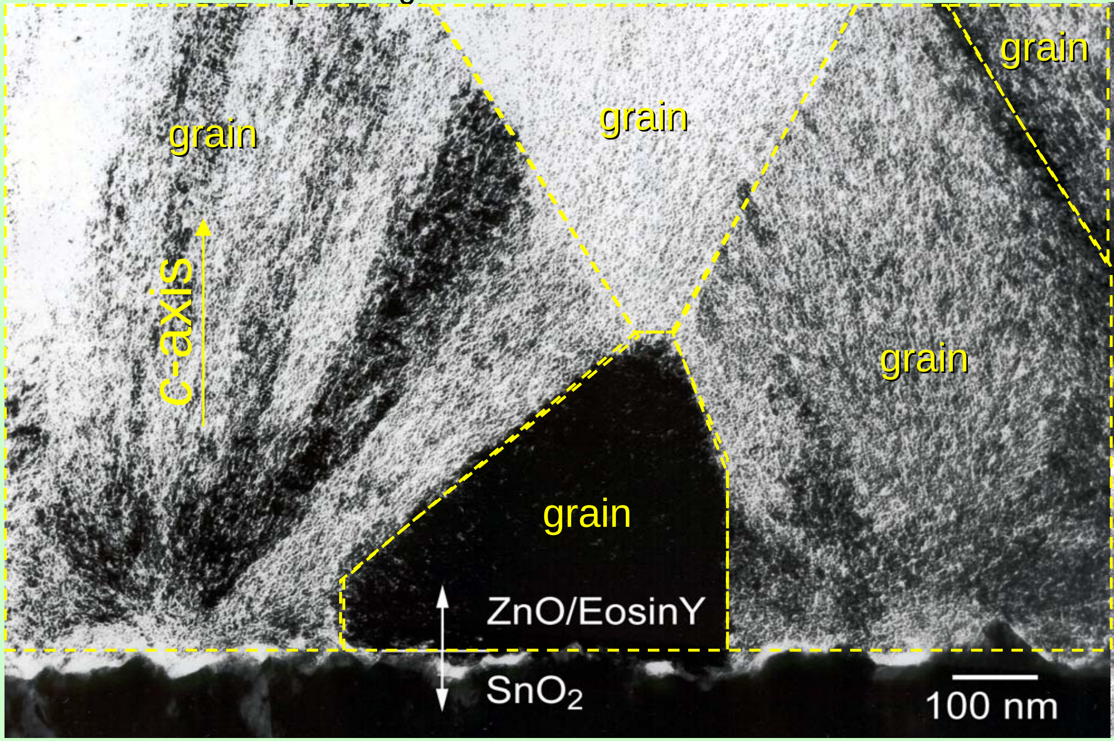
Electron transport in **electrodeposited ZnO** is **faster than in the nanoparticulate ZnO**

T. Oekermann, T. Yoshida, H. Minoura, K.G.U. Wijayantha, L.M. Peter, *J. Phys. Chem. B* **2004**, *108*, 8364.

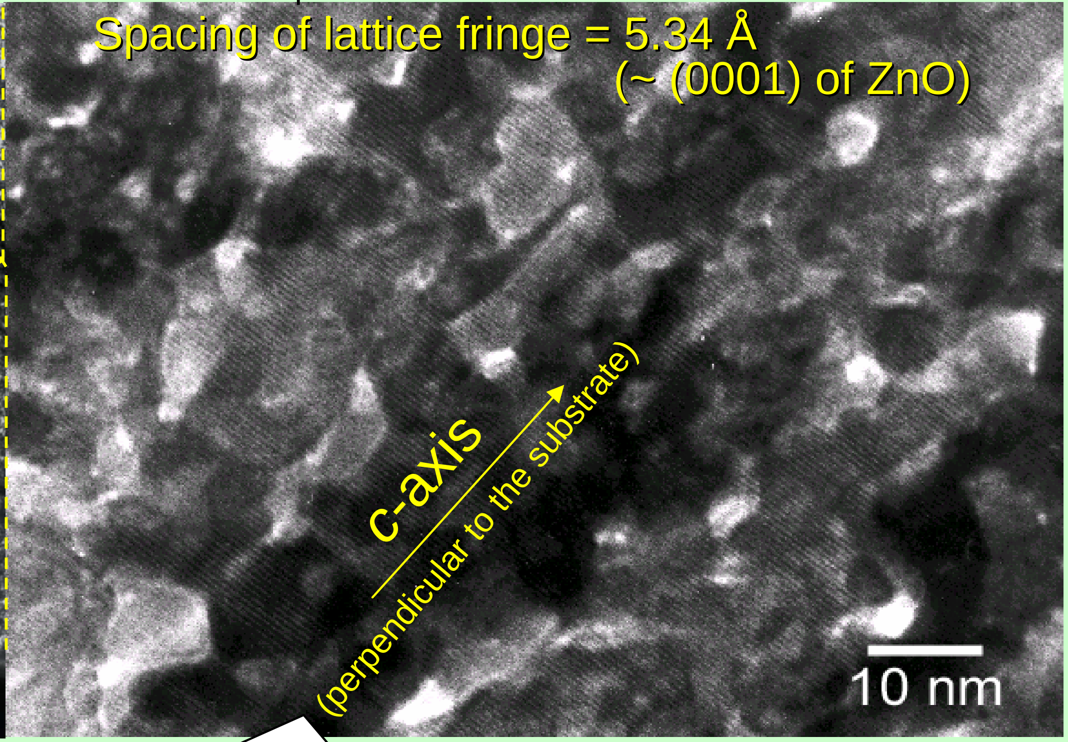
Electron transport model

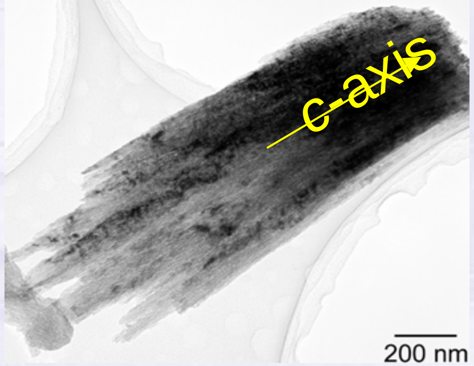
Film deposited at –1.1V (reduced eosinY) on SnO_2 from O_2-saturated $ZnCl_2$ solution

Low mag.; large grains in which fine fibrous pattern spreading outwards from nucleation centers



High mag.; uniform lattice fringes with no correspondence to the fibrous patterns

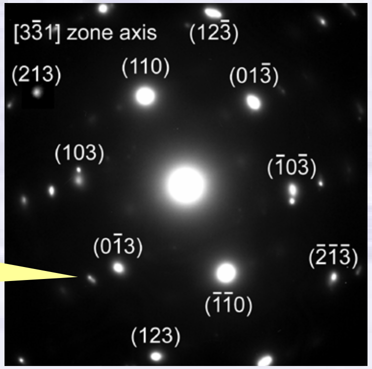

Spacing of lattice fringe = 5.34 Å
(~ (0001) of ZnO)



Orientation independent of porous structure !!!

Spot pattern assignable with one zone axis

“Porous Single Crystal”

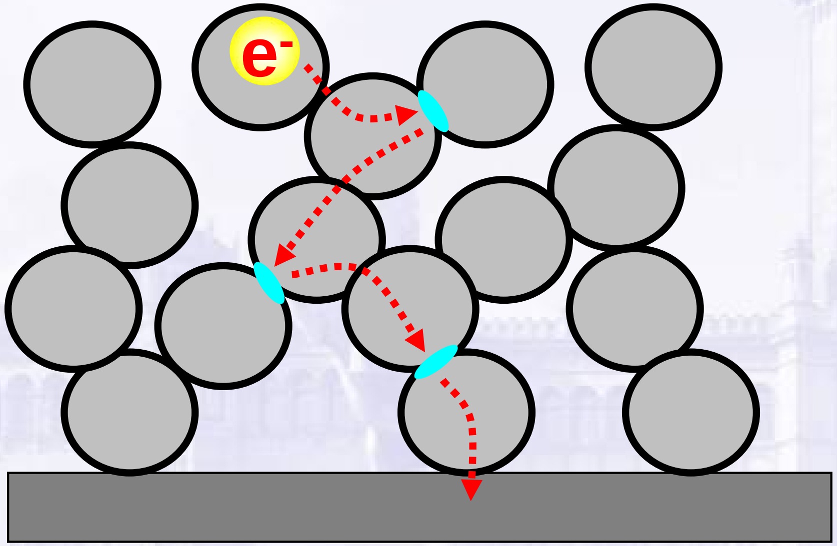


T. Yoshida, T. Pauporte, D. Lincot, T. Oekermann, H. Minoura, *J. Electrochem. Soc.* **2003**, *150*, C608.

Electron transport model

Colloid-processed film made from nanoparticles

Nanocrystalline film

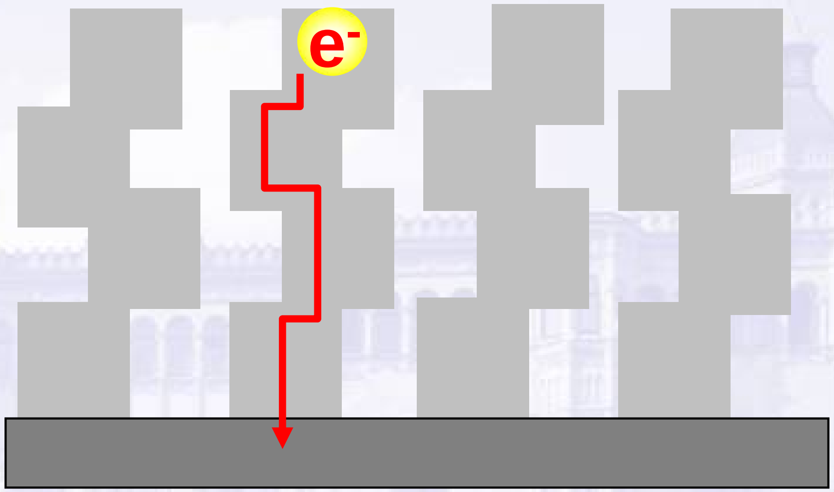


- grain boundaries
- electron traps (●)

Slow electron transport

Electrodeposited film = „Porous single crystal“

Nanoporous film



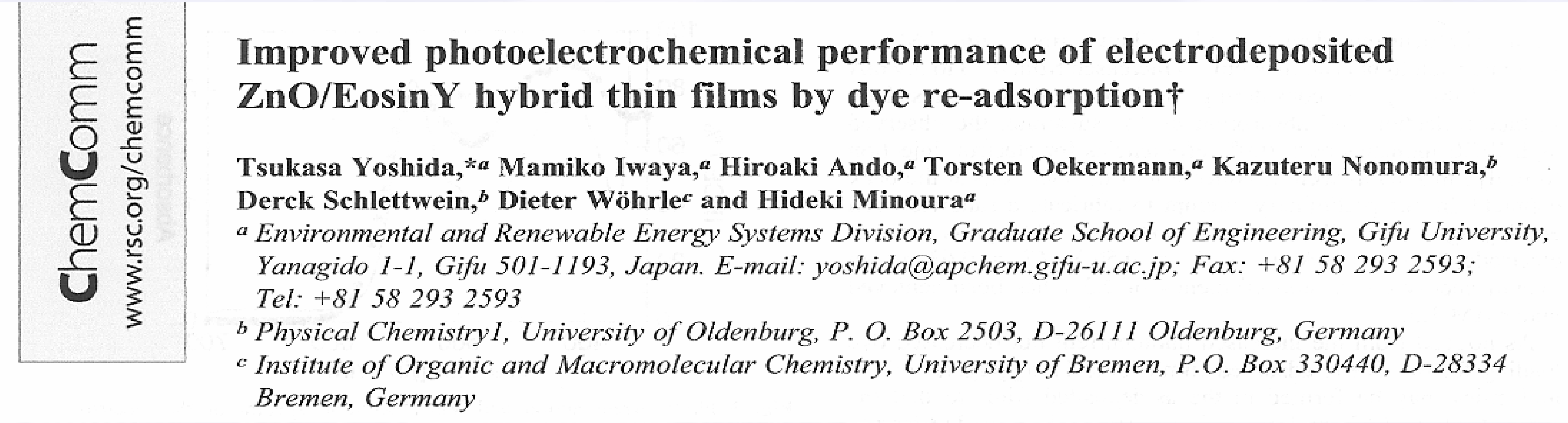
- **No** grain boundaries
- ordered structure

Fast electron transport

→ High electron collection efficiency (not much loss of electrons by recombination during transport through the porous layer)

T. Oekermann, T. Yoshida, H. Minoura, K.G.U. Wijayantha, L.M. Peter, *J. Phys. Chem. B* **2004**, *108*, 8364.

Increase in efficiency by dye re-adsorption



ChemComm

www.rsc.org/chemcomm

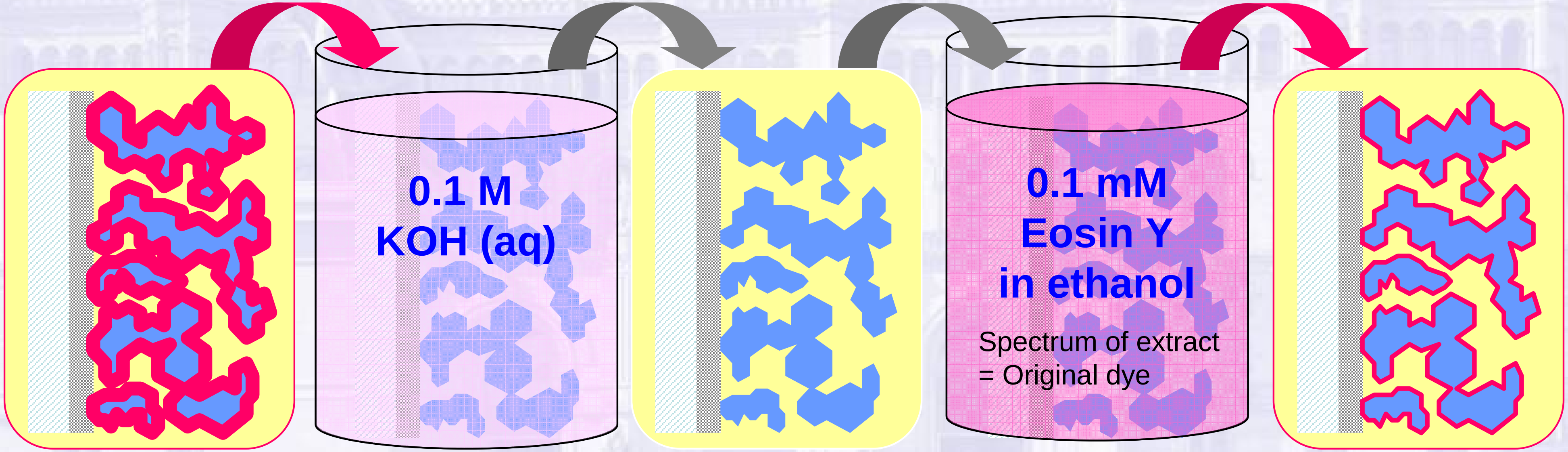
Improved photoelectrochemical performance of electrodeposited ZnO/EosinY hybrid thin films by dye re-adsorption†

Tsukasa Yoshida,*[a] Mamiko Iwaya,[a] Hiroaki Ando,[a] Torsten Oekermann,[a] Kazuteru Nonomura,[b] Derck Schlettwein,[b] Dieter Wöhrle[c] and Hideki Minoura[a]

[a] *Environmental and Renewable Energy Systems Division, Graduate School of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan. E-mail: yoshida@apchem.gifu-u.ac.jp; Fax: +81 58 293 2593; Tel: +81 58 293 2593*

[b] *Physical Chemistry1, University of Oldenburg, P. O. Box 2503, D-26111 Oldenburg, Germany*

[c] *Institute of Organic and Macromolecular Chemistry, University of Bremen, P.O. Box 330440, D-28334 Bremen, Germany*



0.1 M KOH (aq)

0.1 mM Eosin Y in ethanol

Spectrum of extract = Original dye

Dye aggregates

Desorption

Porous ZnO film

Re-adsorption

Dye monolayer

T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.* **2004**, 400.

Increase in efficiency by dye re-adsorption

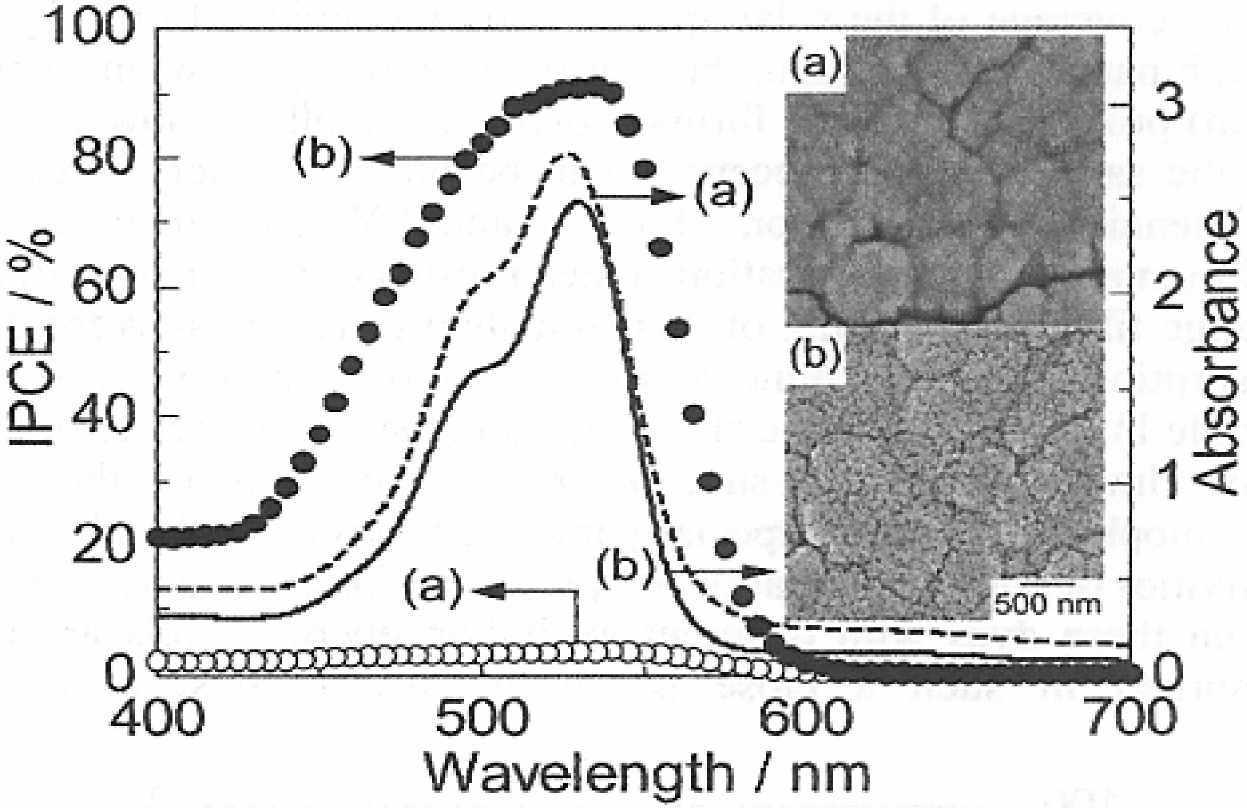
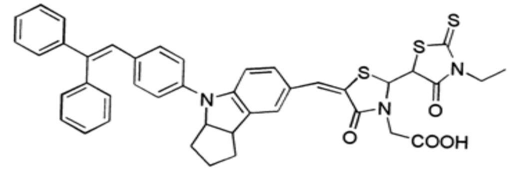


Fig. 1 Surface SEM photographs, Vis absorption spectra and photocurrent action spectra of as-deposited (a) and dye re-adsorbed (b) ZnO/eosinY hybrid thin films.

- Decrease in absorption

- IPCE ca. 90 % in the abs. maximum (before re-adsorption: around 50 %)

- SEM: Film becomes more porous after re-adsorption !



D149

Efficiency
- before re-adsorption: 0.8 %
- after re-adsorption: 2.3 %

➡ **Even higher efficiencies using dye with broader light absorption.**
Current record: D149 dye
5.8 % at 1 sun (AM1.5)

T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.* **2004**, 400.

Use of other structure-directing agents

- Re-adsorption of the (same or another) dye has to be done anyway

→ *Use of other kinds of organic molecules is possible*

→ *Broader range of molecules available for further optimization of film porosity, surface area, electron transport and back reaction properties etc.*

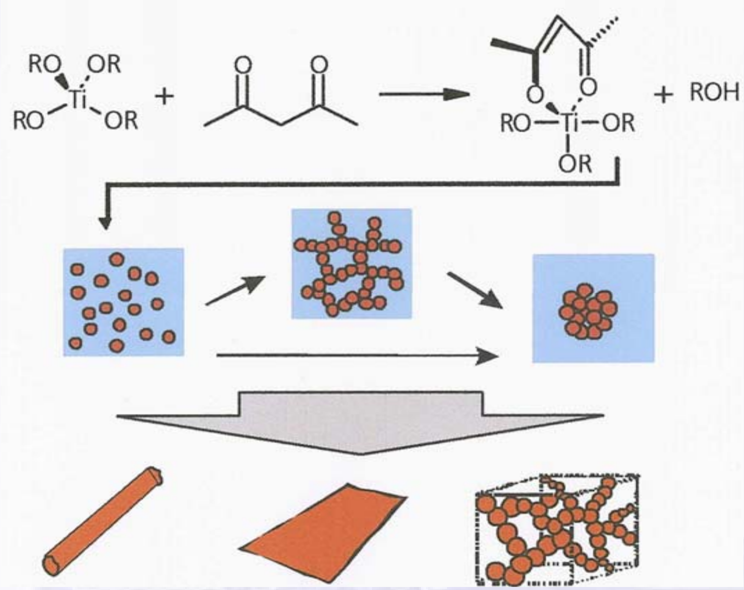
- In addition: Find out principles of structure-directing in the electrodeposition of metal oxides

→ Use of

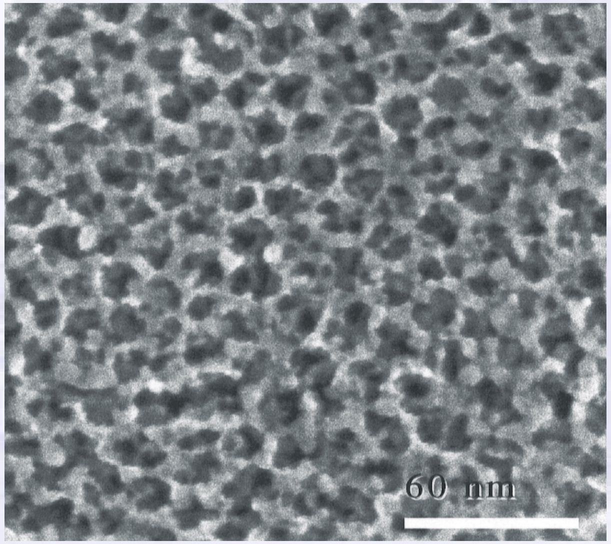
- Surfactants (often used for preparation of porous metal oxide films by sol-gel methods)

- Sugar molecules

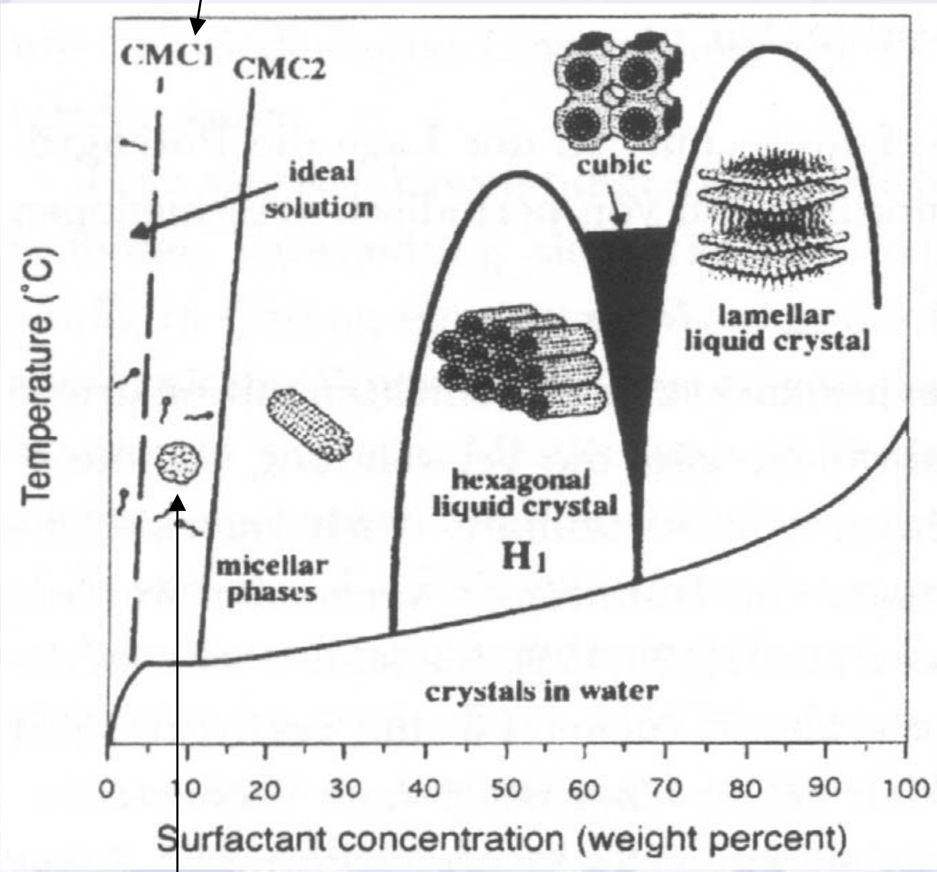
Use of surfactants in film preparation by sol-gel method



Sol-gel process



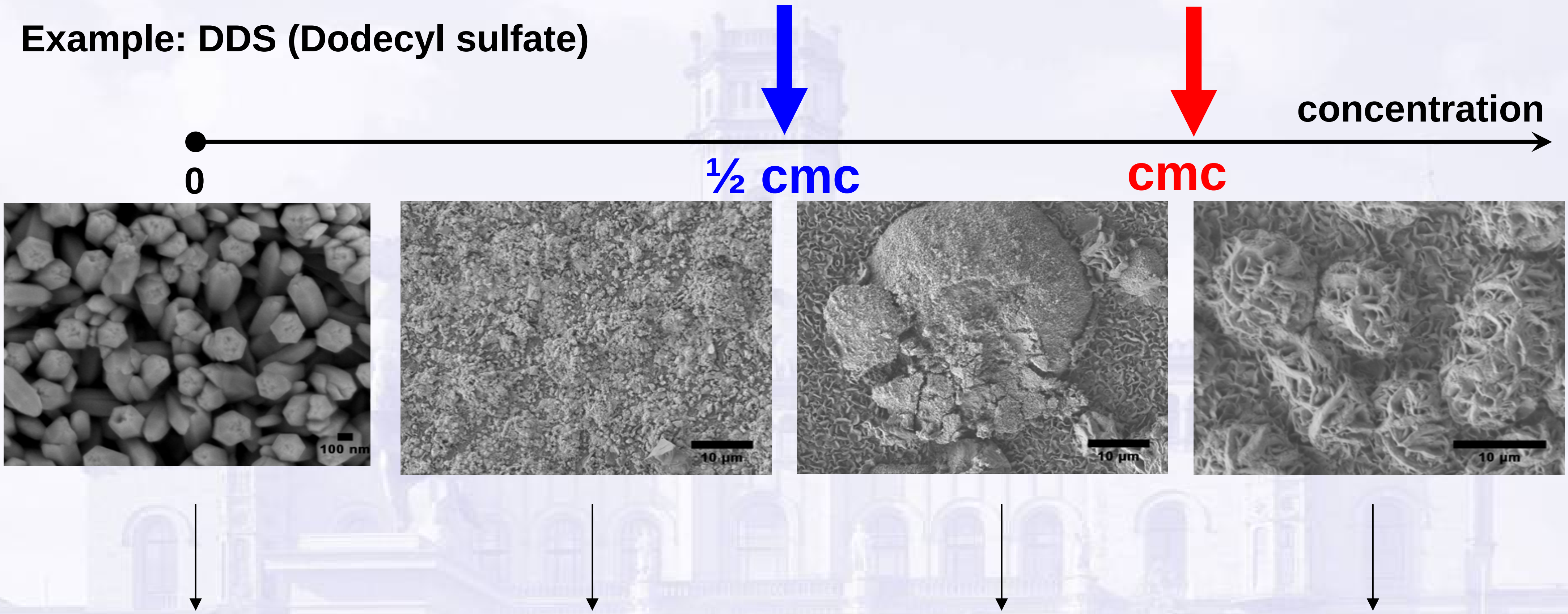
CMC =
Critical micelle concentration



Formation of
spherical micelles

Two ZnO phases depending on surfactant concentration

Example: DDS (Dodecyl sulfate)



concentration

0

½ cmc

cmc

without surfactant

Hexagonal ZnO crystals

far below cmc

Nano-particles

near but below cmc

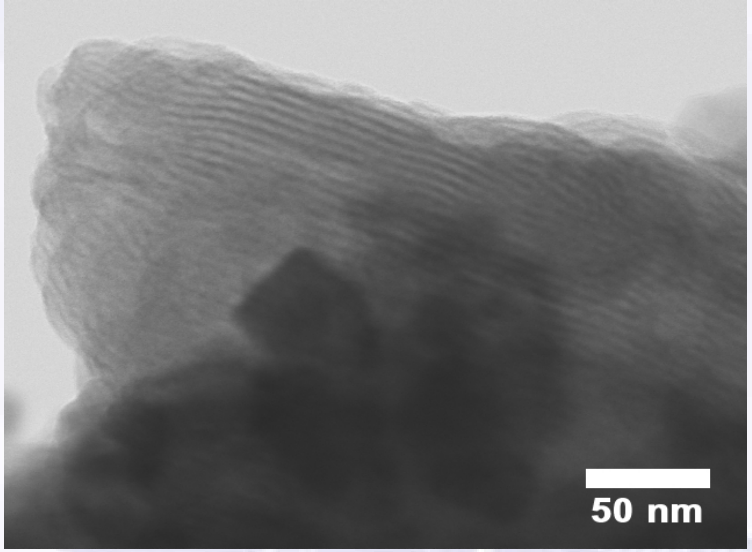
Both Phases

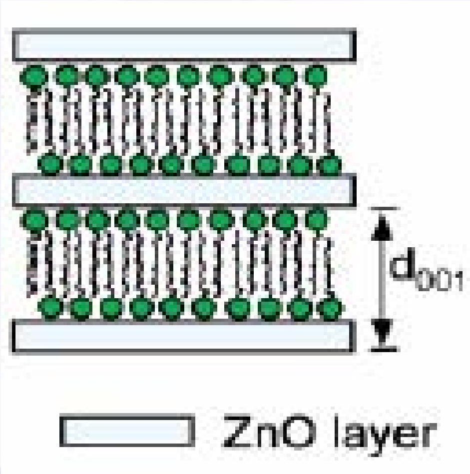
above cmc

Disc-like Particles

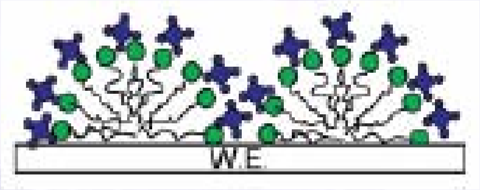
C. Boeckler, A. Feldhoff, M. Wark, T. Oekermann, *Langmuir* **2006**, *22,* 9427.

Lamellar phase (formed at high surfactant concentration)

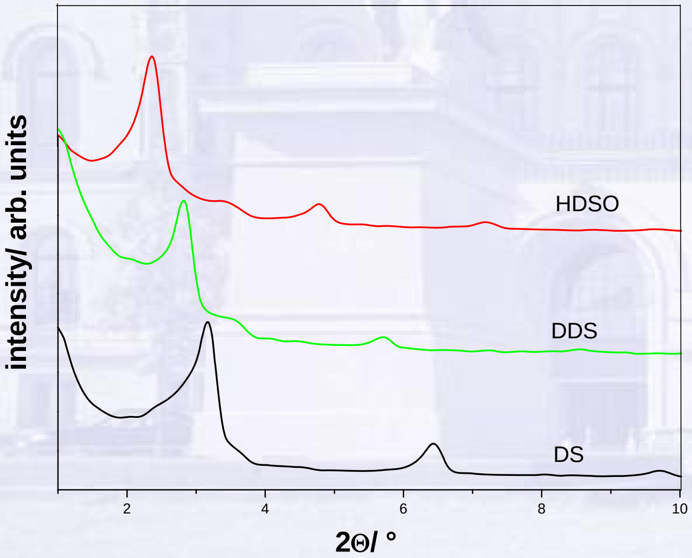


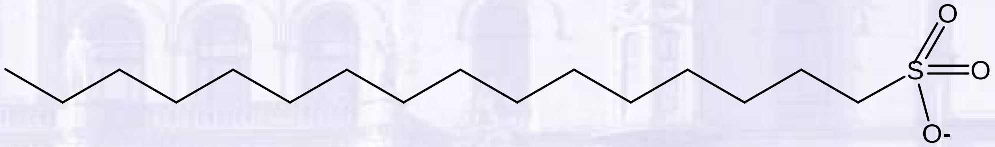


**> ½ cmc:
Formation of
surface micelles***

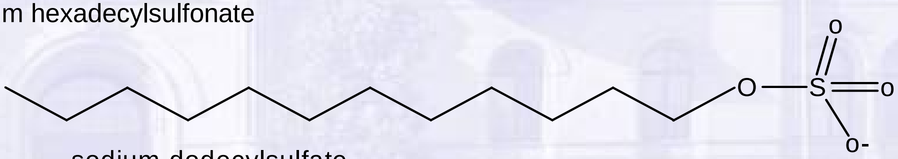


Low angle XRD

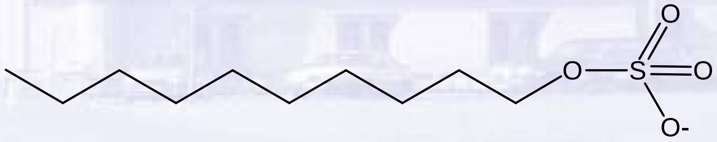




sodium hexadecylsulfonate



sodium dodecylsulfate

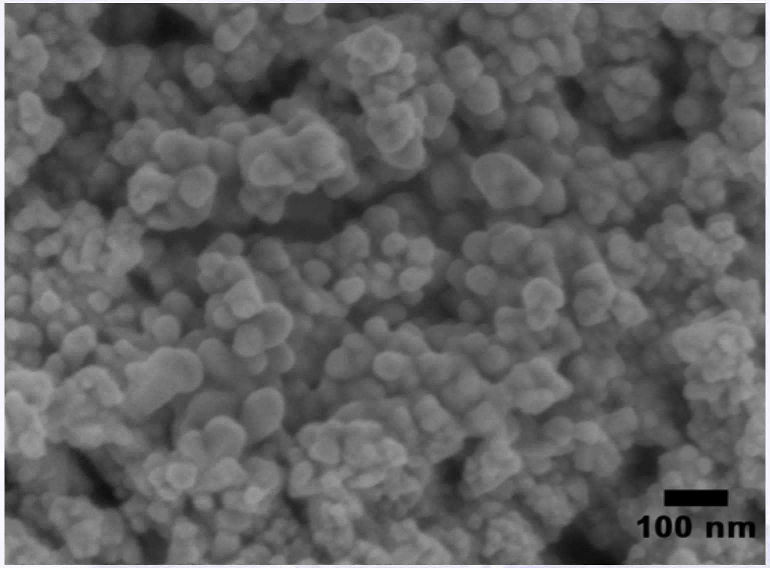


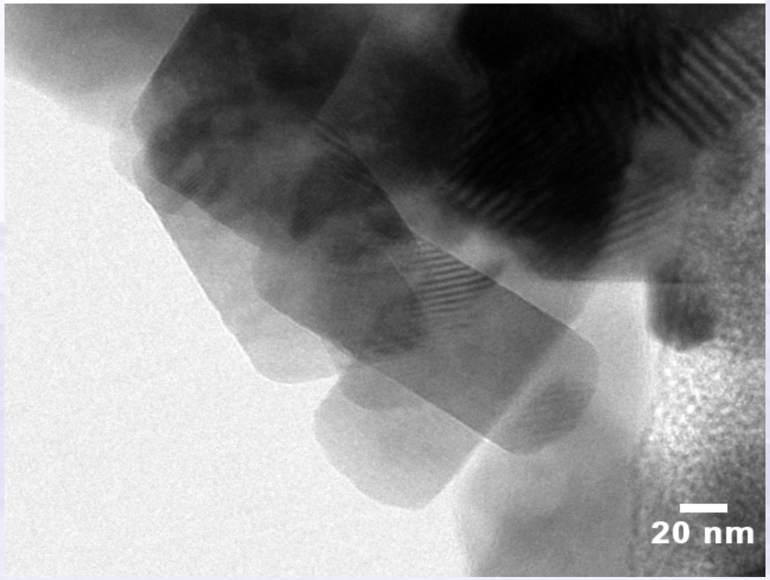
sodium decylsulfate

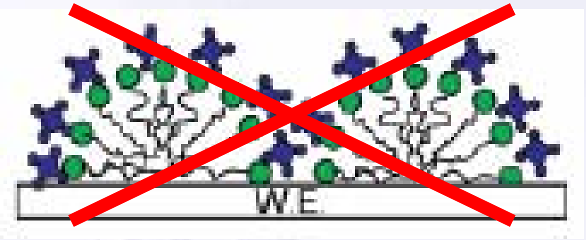
C. Boeckler, A. Feldhoff, M. Wark, T. Oekermann, *Langmuir* **2006***, 22,* 9427.

* Liu, J.F.; Ducker, W.A. *J. Phys. Chem. B* **1999**, *103*, 8558

Nanoparticulate phase (formed at low surfactant conc.)

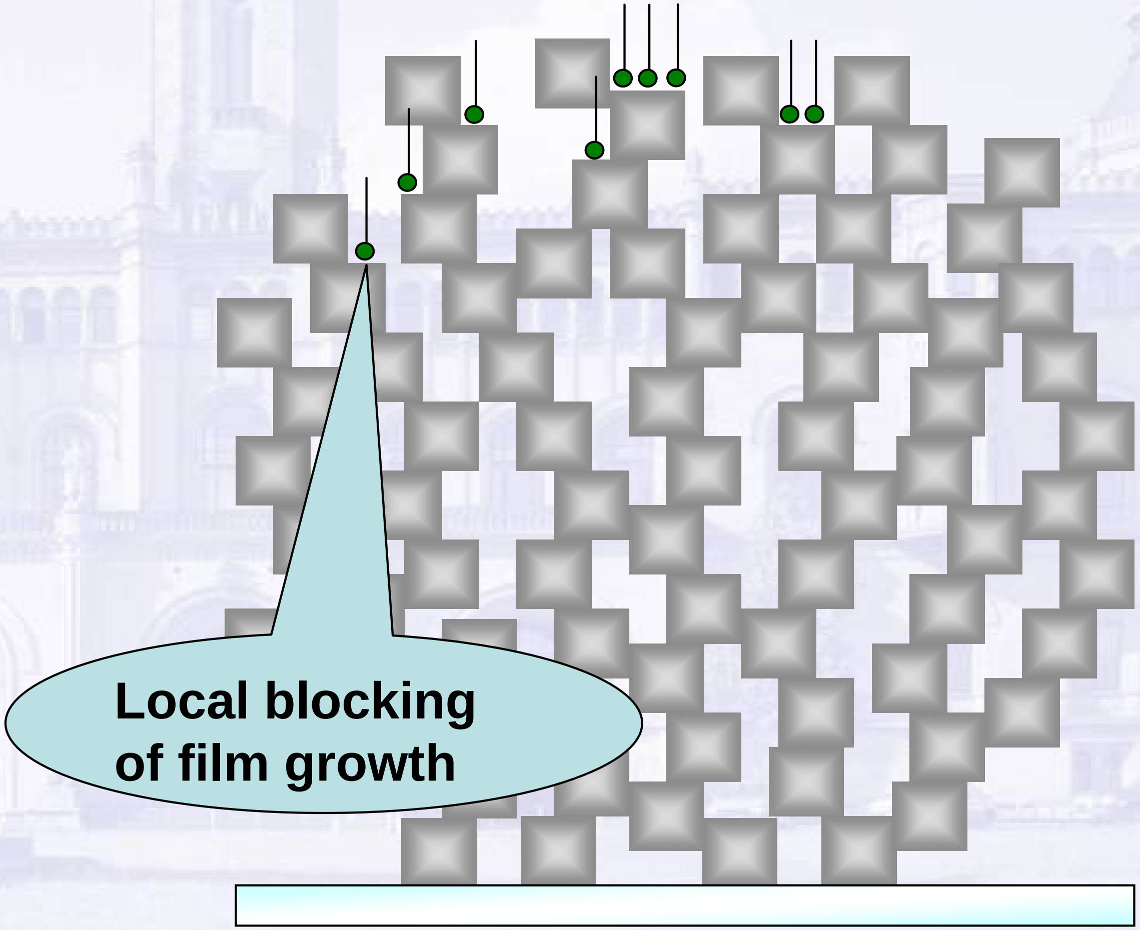






< ½ cmc:
No surface micelles

No sulfur in the films (EDXS)

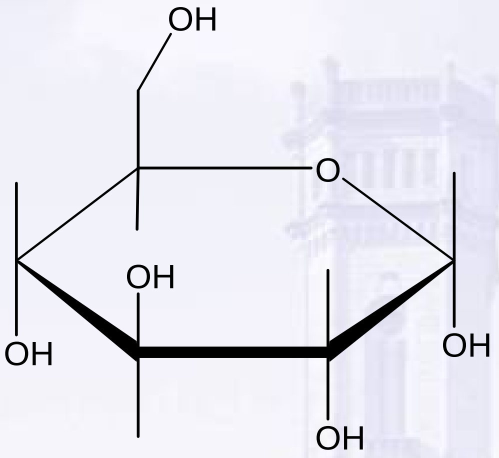


Local blocking of film growth

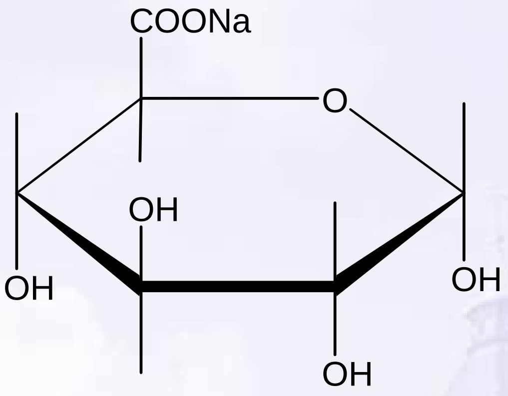
C. Boeckler, A. Feldhoff, M. Wark, T. Oekermann, *Langmuir* **2006**, *22,* 9427.

Sugar molecules as structure directors

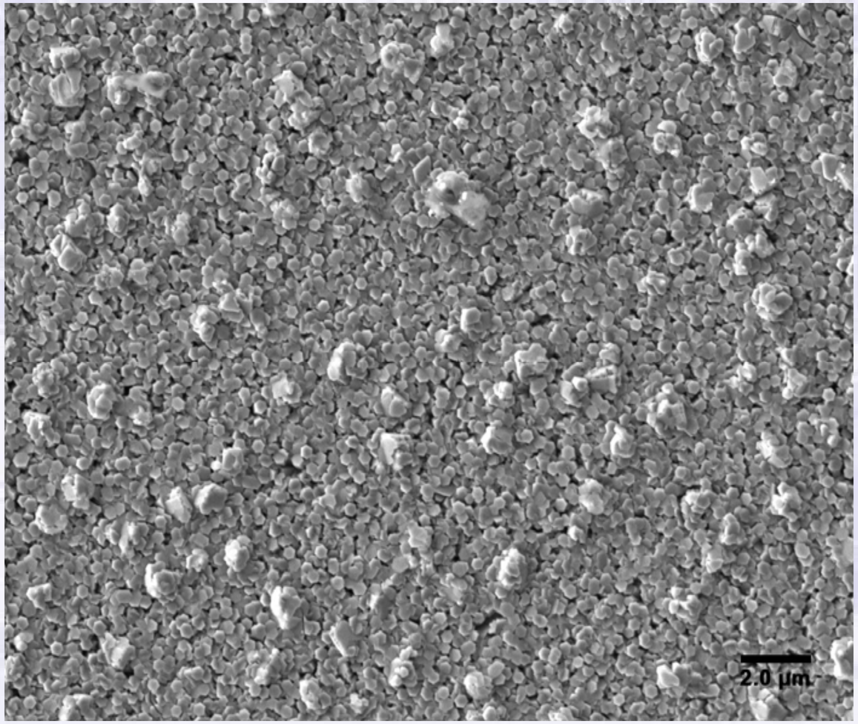
Sugar molecules:
- Easily available in many variations
- Monomers, dimers, oligomers
- Can easily be modified (functional groups)

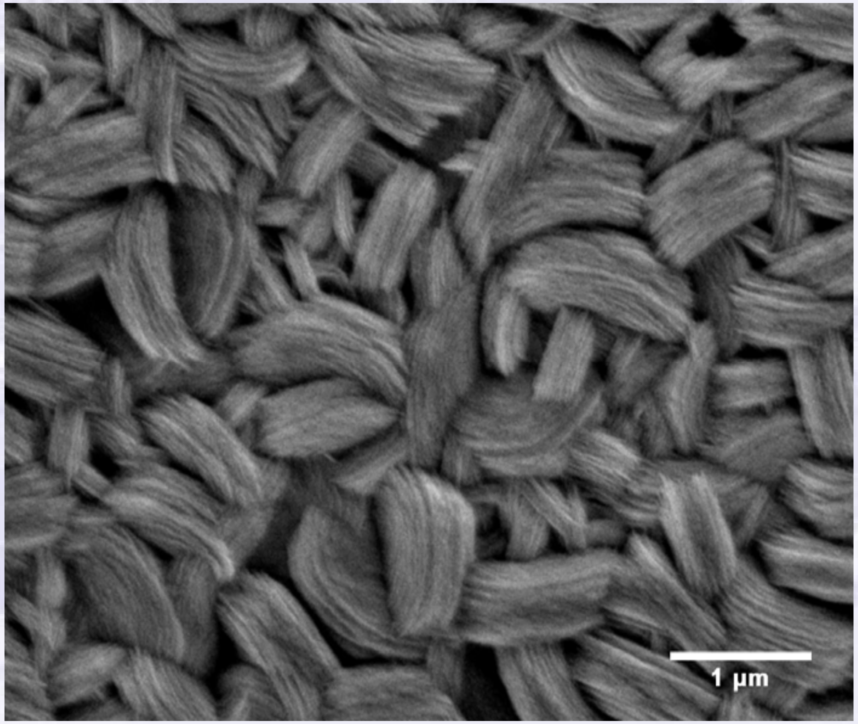


glucose



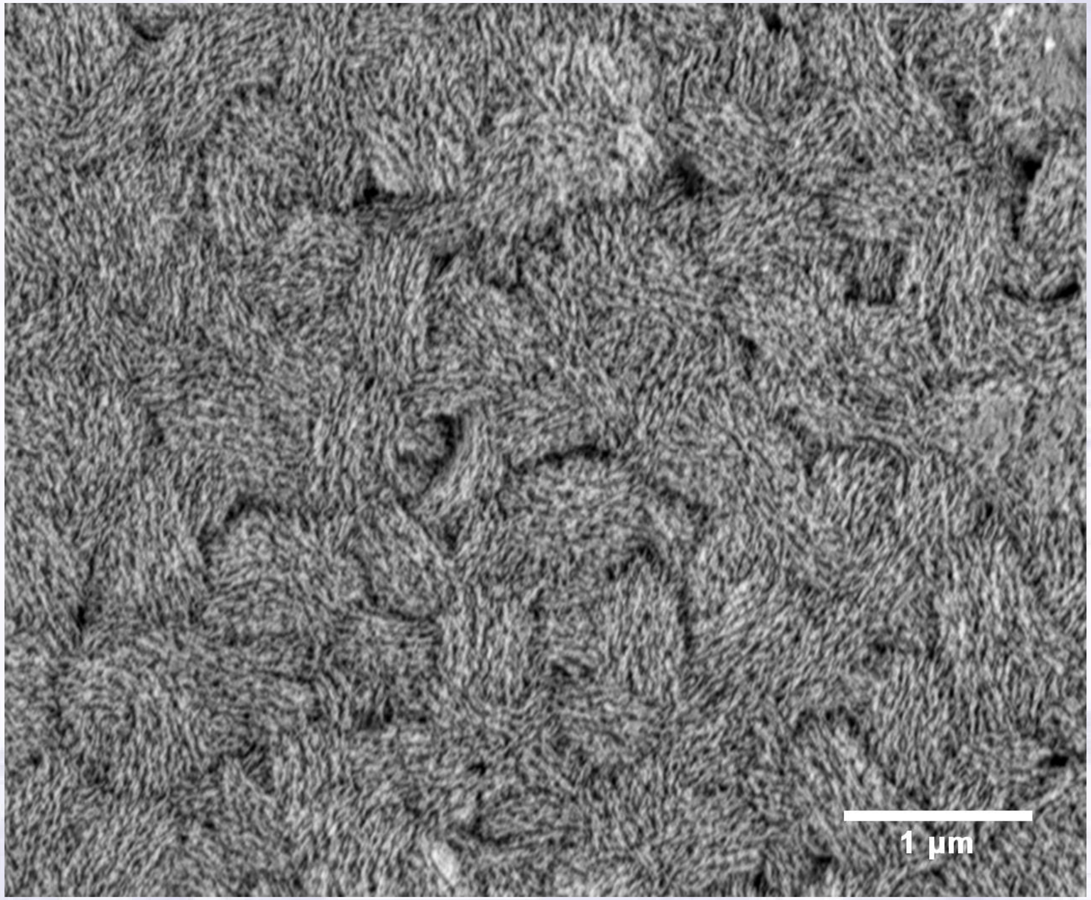
sodium glucuronic acid

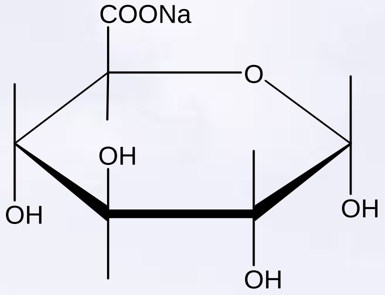




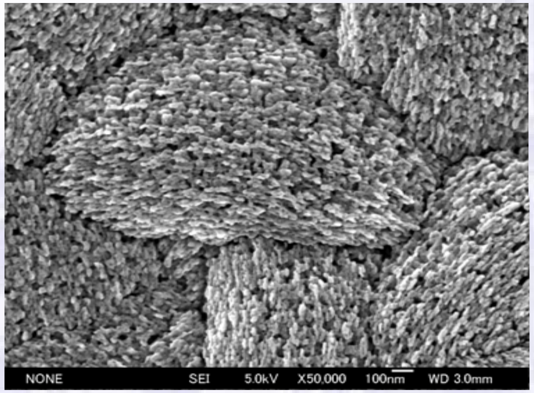
Higher concentration of glucoronic acid

1 mM instead of 0.5 mM → porous film !





sodium glucuronic acid



Similar porosity as films templated with eosin Y ! (But at much higher concentration !)

→ Re-adsorption of dye molecules and test in dye-sensitized solar cells (not performed yet)

Electrodeposition of TiO_2

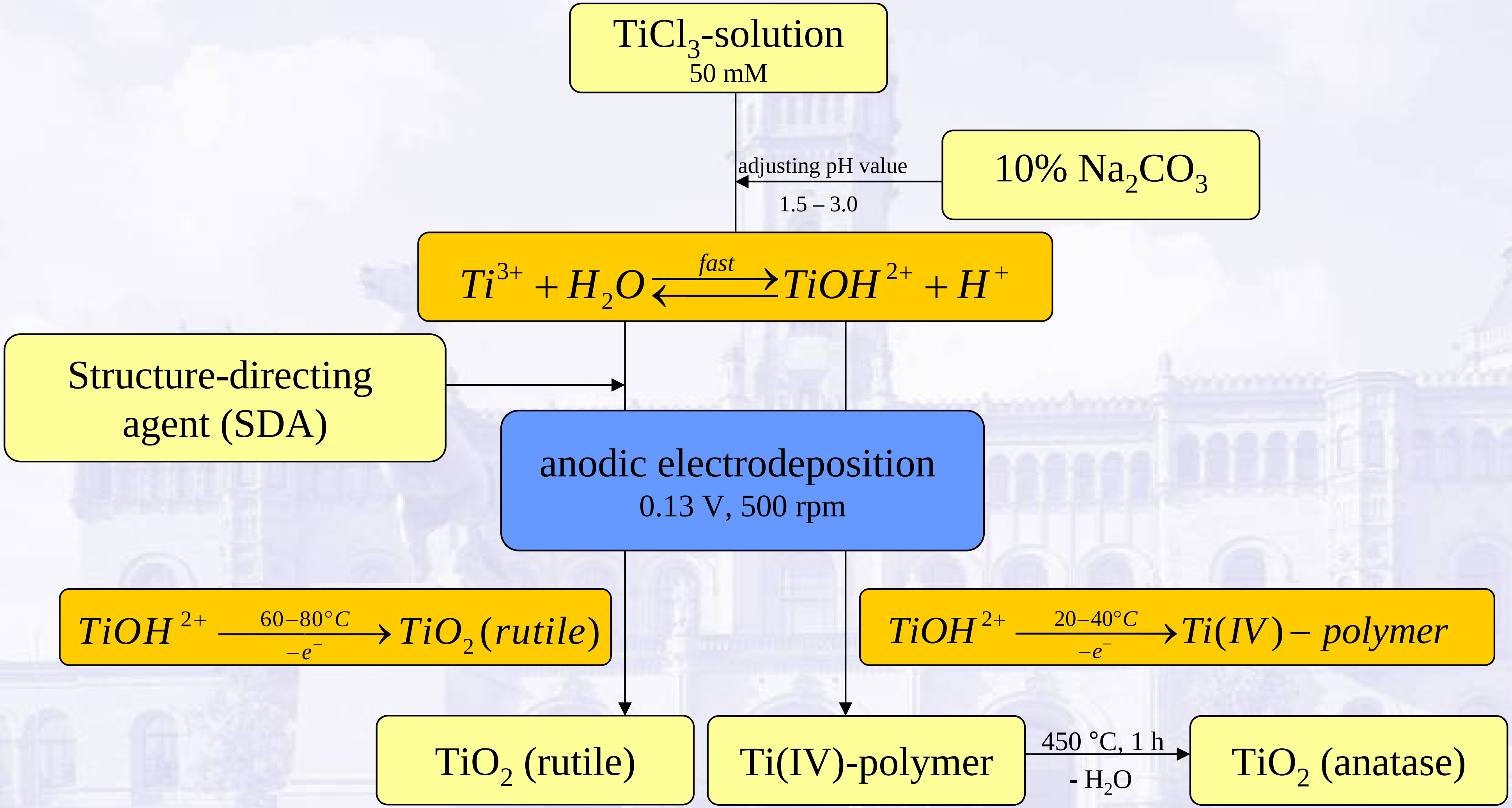
- Good electron transport properties for **electrodeposited ZnO** film
- Nanoparticulate TiO_2 films more efficient than nanoparticulate ZnO

→ **Electrodeposition of TiO_2 is desirable !**

Problem:
- No direct electrodeposition of crystalline TiO_2 realized yet
- Deposition of Ti-oxo-hydroxide, which must be calcined to obtain TiO_2
- Films are not porous

→ **Modification of known methods for TiO_2 deposition**

Electrodeposition of TiO_2 from $TiCl_3$-Solution



$TiCl_3$-solution
50 mM

adjusting pH value
1.5 – 3.0

10% Na_2CO_3

$$Ti^{3+} + H_2O \overset{fast}{\rightleftarrows} TiOH^{2+} + H^{+}$$

Structure-directing agent (SDA)

anodic electrodeposition
0.13 V, 500 rpm

$$TiOH^{2+} \xrightarrow[-e^{-}]{60-80°C} TiO_2(rutile)$$

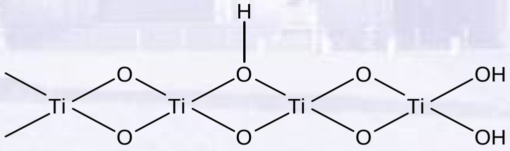
$$TiOH^{2+} \xrightarrow[-e^{-}]{20-40°C} Ti(IV) - polymer$$

TiO_2 (rutile)

Ti(IV)-polymer

450 °C, 1 h
- H_2O

TiO_2 (anatase)



L. Kavan, B. O´Regan, A. Kay, M. Grätzel, J. *Electroanal. Chem.*, **346** (1993) 291.
L. Kavan, M. Zukalova, M. Kalbáč, M. Grätzel, *J. Electrochem. Soc.*, **151** (2004) 1.

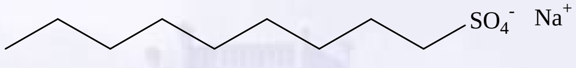
Structure-directing agents (SDA) for TiO_2 deposition


calcined film

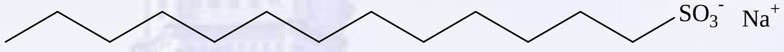
as deposited

film after dipping in basic solution

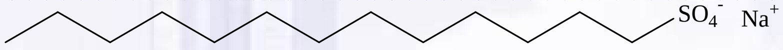
film deposited with BTB at 80 °C



Natriumoctylsulfat (NOS) $C_8H_{17}SO_4Na$

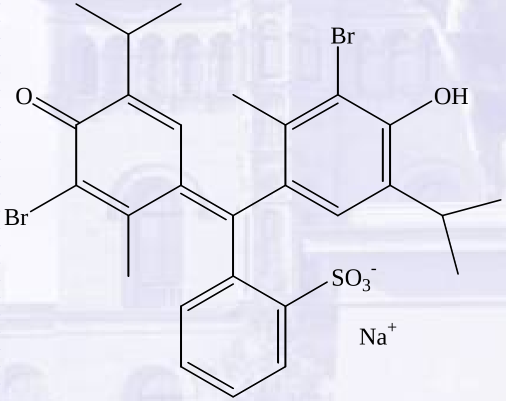


Dodecansulfonat $C_{12}H_{25}SO_3Na$



Sodiumdodecylsulfat (SDS) $C_{12}H_{25}SO_4Na$

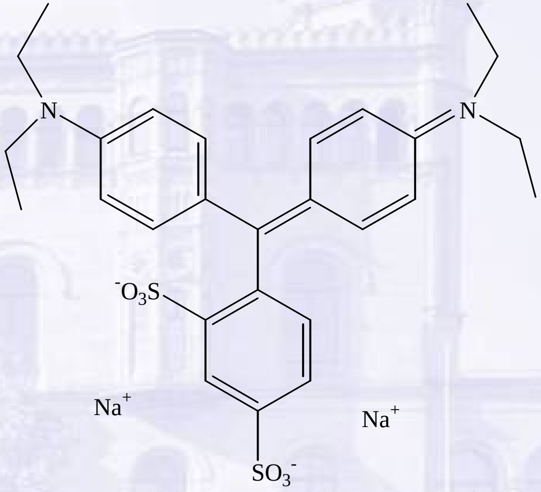

film deposited with SDS at 80 °C



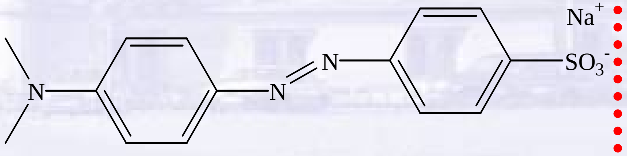
Bromthymolblau (BTB)

Co-deposition of different SDA at different temperatures

SDA	20 °C	80 °C
SDS	✓	✓
BTB	✓	✓
Na-octylsulfate	X	X
disulfin blue	X	✓
dodecansulfuric acid	X	✓
methylorange	X	X



Disulfinblau

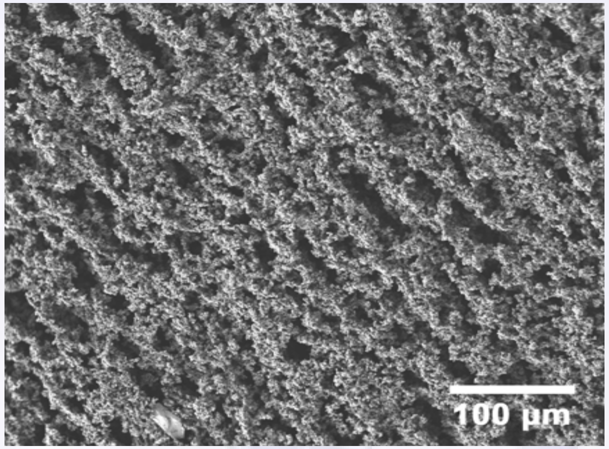


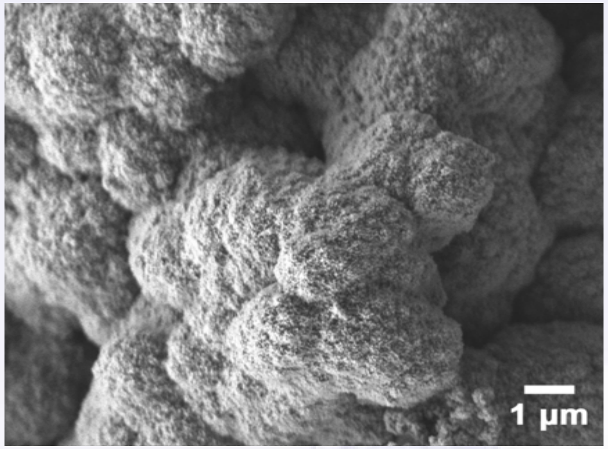
Methylorange

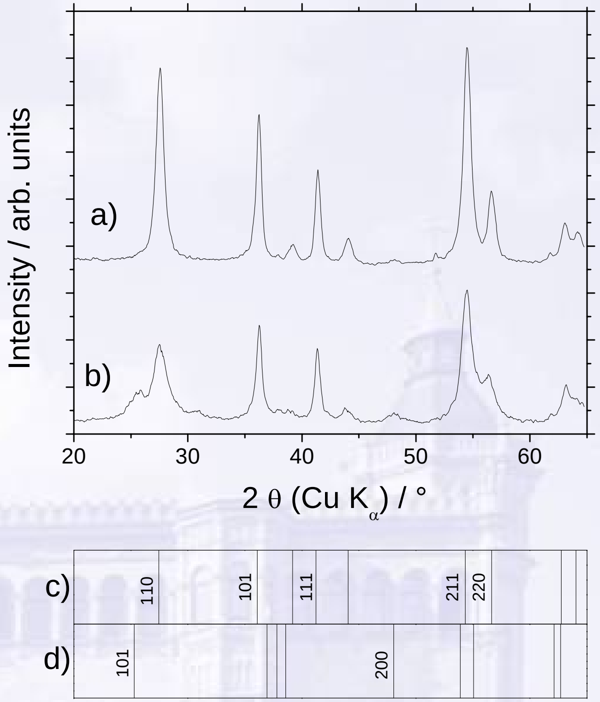
K. Wessels, A. Feldhoff, M. Wark, J. Rathousky, T. Oekermann, *Electrochem. Solid-State Lett*. **2006**, *9*, C93.
K. Wessels, M. Maekawa, J. Rathousky, T. Oekermann, *Thin Solid Films*, submitted.
J. Rathousky, K. Wessels, M. Wark, T. Oekermann, *Stud. Surf. Sci. Catal.*, submitted.

Leibniz Universität Hannover

Direct electrodeposition of crystalline TiO_2







a) calcined film, deposited with SDS

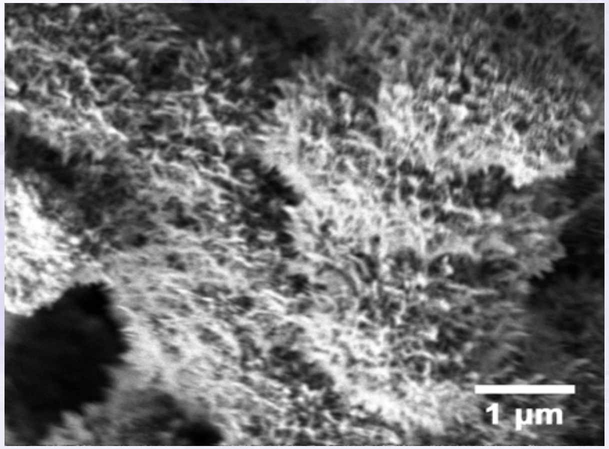
b) as deposited film

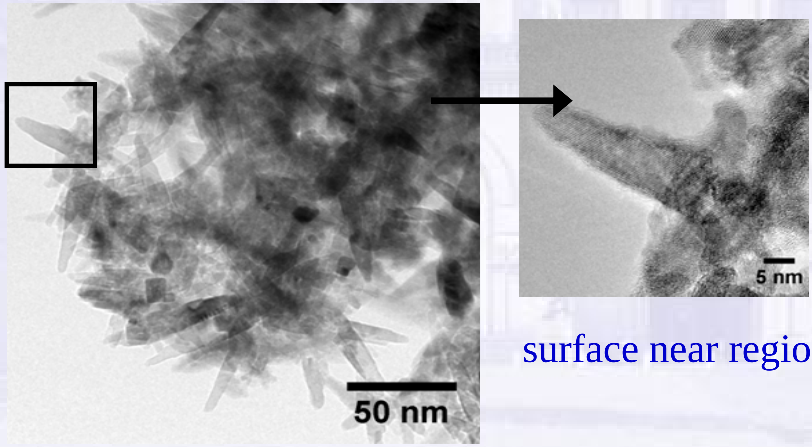
c) reference data rutile [1]

d) reference data anatase [1]

Deposition of crystalline nanoparticulate film at 60-80°C !
(With SDS and BTB)

TEM





surface near region

→ **Rutile is formed**

K. Wessels, A. Feldhoff, M. Wark, J. Rathousky, T. Oekermann, *Electrochem. Solid-State Lett*. **2006**, *9*, C93.
K. Wessels, M. Maekawa, J. Rathousky, T. Oekermann, *Thin Solid Films*, submitted.
J. Rathousky, K. Wessels, M. Wark, T. Oekermann, *Stud. Surf. Sci. Catal.*, submitted.

Efficiency of electrodeposited TiO_2 in DSSC

Efficiency in DSSC

TiO_2-film agent, reaction time film thickness	treatment	amount of adsorbed dye N_3 nmol/cm^2	dye concentration mol/L	η / %
SDS, 2 h 30 µm	calcined 450 °C, 1 h	261,3	0,087	0,068
	desorbed 24 h EtOH	123,4	0,041	0,011
	untreated	106,7	0,036	0,015
SDS, 30 min 15 µm	calcined 450 °C, 1 h	310,6	0,207	**0,789**
	desorbed 24 h EtOH	13,23	0,009	0,070
	untreated	92,57	0,062	**0,078**
BTB, 2 h 160 µm	calcined 450 °C, 1 h	560,4	0,035	0,333
	desorbed 24 h EtOH	59,43	0,004	0,013
	untreated			0,020

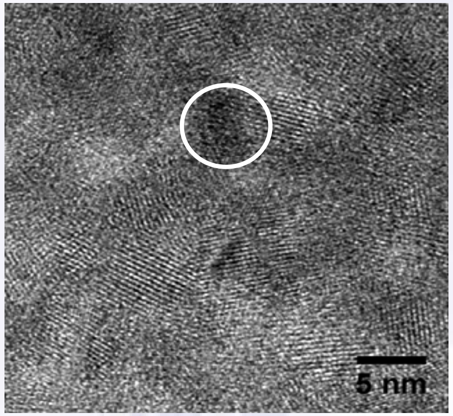
- calcination increases dye adsorption and efficiency
- thinner films show higher efficiency

DSSC dye sensitized solar cells

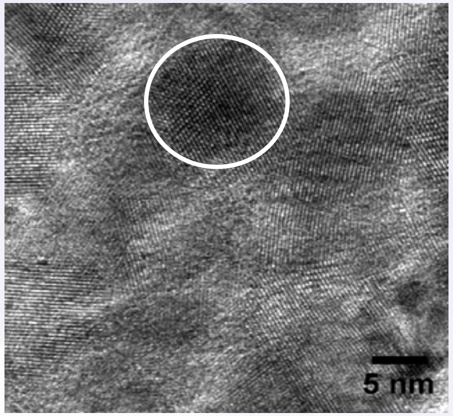
K. Wessels, A. Feldhoff, M. Wark, J. Rathousky, T. Oekermann, *Electrochem. Solid-State Lett*. **2006**, *9*, C93.
K. Wessels, M. Maekawa, J. Rathousky, T. Oekermann, *Thin Solid Films*, submitted.
J. Rathousky, K. Wessels, M. Wark, T. Oekermann, *Stud. Surf. Sci. Catal.*, submitted.

Effect of calcination on electrodeposited TiO_2

particle size (nm)	XRD (Scherrer eq.)	TEM
as deposited film	5,8	5
calcined film	10,2	10



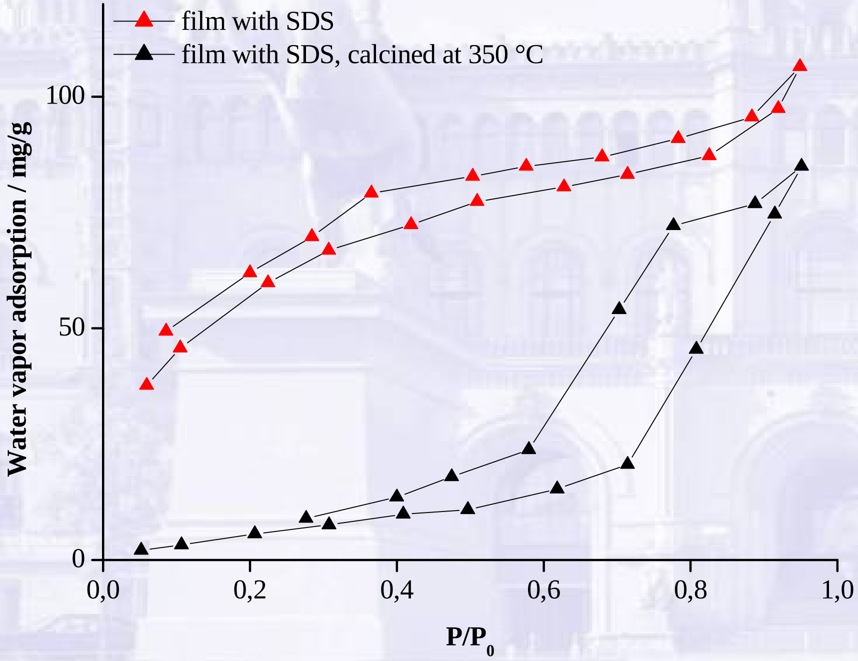
as deposited film



calcined film

Scherrer equation

$$\boxed{D = \frac{K\lambda}{\beta_L \cos\theta}}$$



water vapor adsorption

- **as deposited films contain micropores and small mesopores** (Ø ≈ 1 - 2 nm, V_{pores} ≈ 20 mm²/g)
- **calcined films contain of a large amount of mesopores** (Ø >5 nm, V_{pores} ≈ 77 mm²/g)

→ Pores in as-deposited film too small for bulky dye molecules ?

K. Wessels, A. Feldhoff, M. Wark, J. Rathousky, T. Oekermann, *Electrochem. Solid-State Lett*. **2006**, *9*, C93.
K. Wessels, M. Maekawa, J. Rathousky, T. Oekermann, *Thin Solid Films*, submitted.
J. Rathousky, K. Wessels, M. Wark, T. Oekermann, *Stud. Surf. Sci. Catal.*, submitted.

Conclusions

- **Highly porous ZnO** films can be **electrodeposited** using **dye molecules** as well as **other organic molecules (e.g. sugar molecules)**

- **Electrodeposited ZnO** films show **superior electron transport properties** compared to nanoparticulate ZnO films, leading to **higher efficiency**

- **Fully crystalline TiO_2** films could be electrodeposited from **$TiCl_3$ solution** at higher temperature (> 60 °C)

- Still low efficiency of electrodeposited TiO_2 due to the **pore size**, which has to be **optimized for use in dye-sensitized solar cells** (using other structure-directing agents, varying concentrations of SDA, etc.)

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Frank Steinbach (technician / TEM)
Kerstin Janze (technician)

Prof. Dr. Jürgen Caro (group leader)
PD Dr. Michael Wark (vice group leader)

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