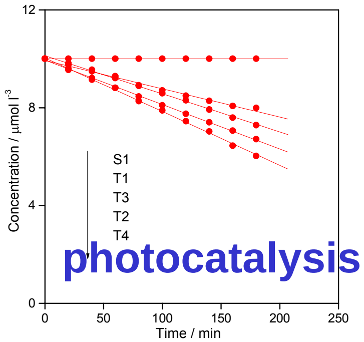
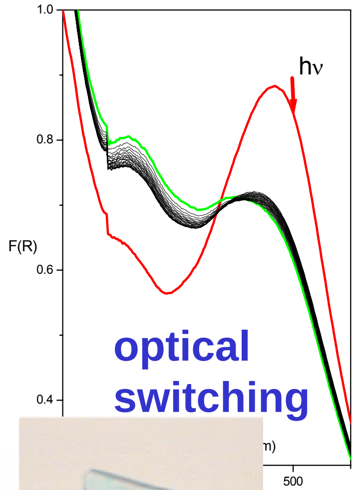
Funktionalisierte nanoporöse Oxide: Synthese und Anwendungsbeispiele

Functionalized nanoporous oxides: synthesis and examples for potential applications

PD Dr. **Michael Wark**

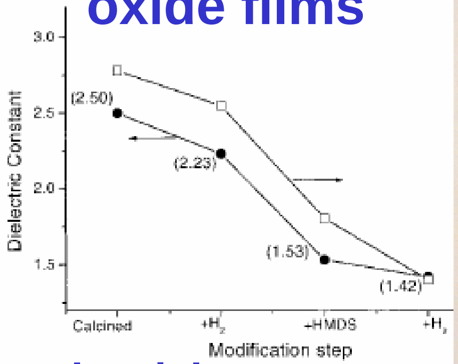


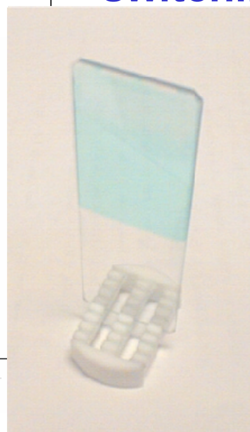
photocatalysis



optical switching

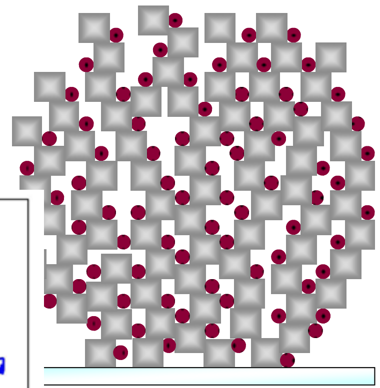
Modified mesoporous oxide films

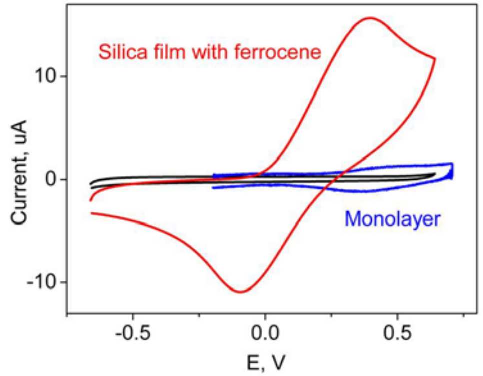




low k layers

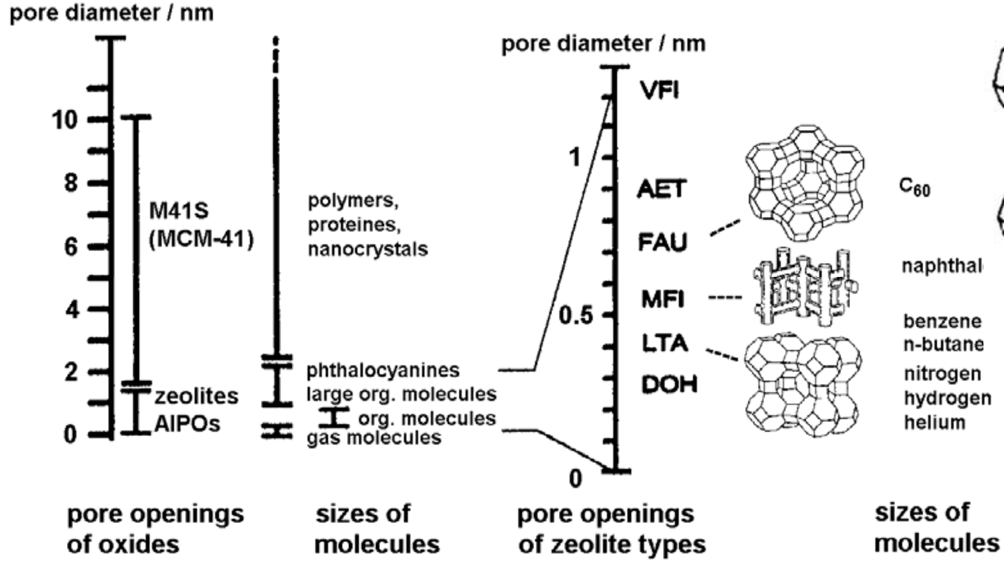
Porous oxide electrodes

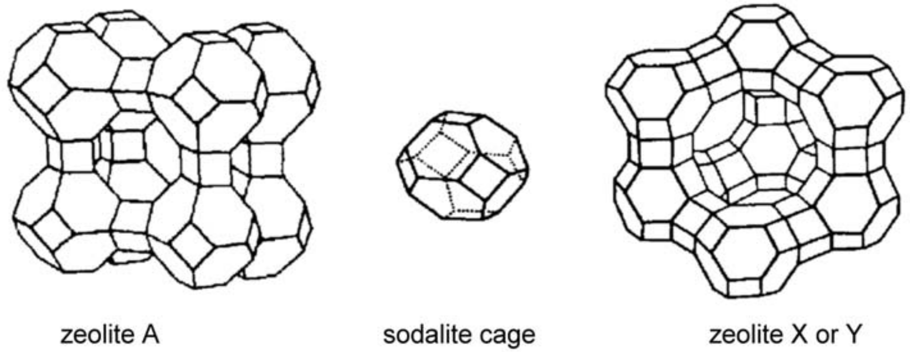


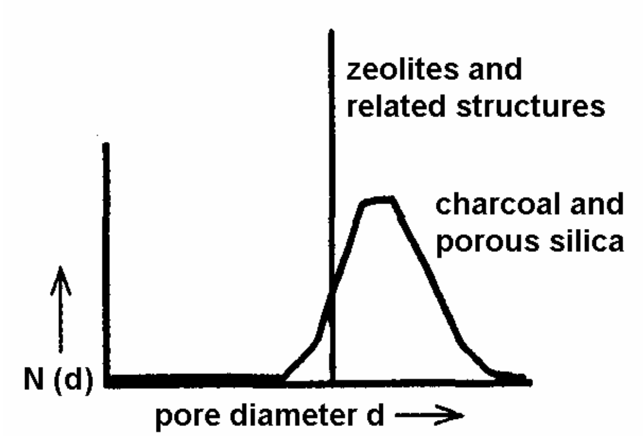


Charge carrier propagation, Solar cells

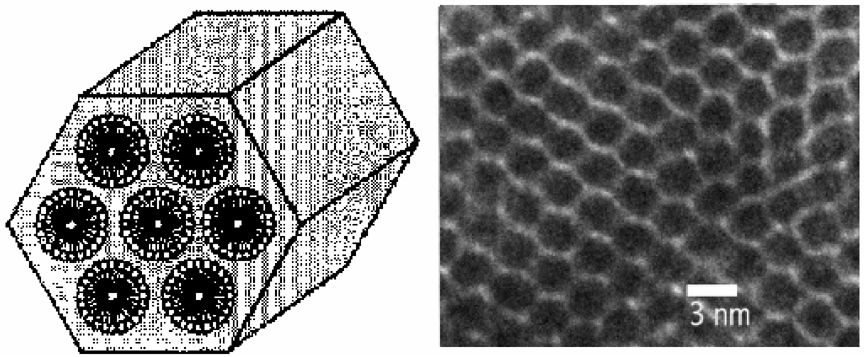
Nanostructured oxidic host materials





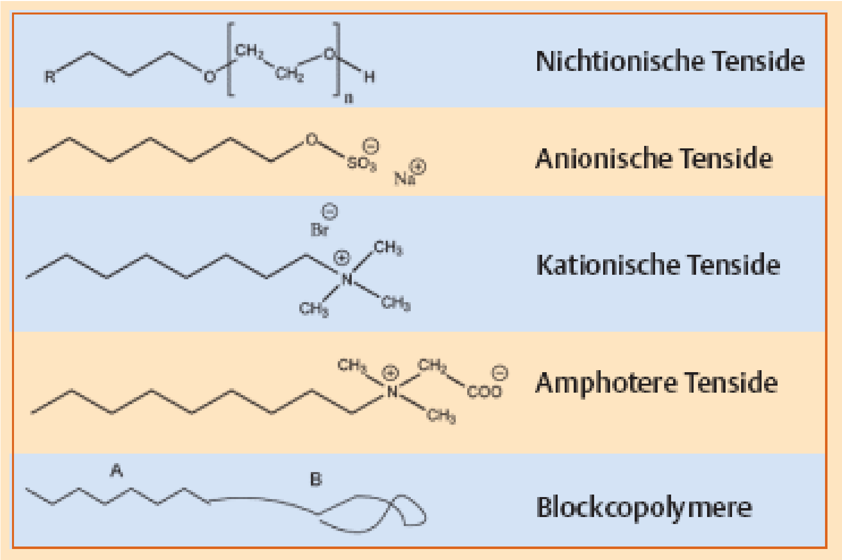


Mesoporous oxides (e.g. SiO_2 of M41S-type)



very high surface areas: about 1000 m^2/g

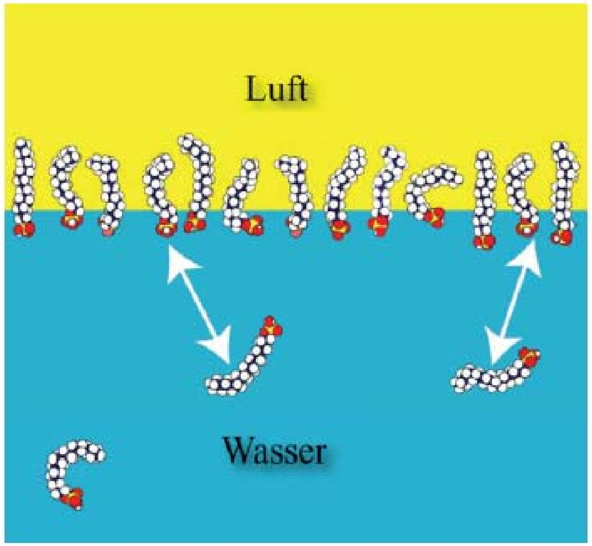
Surfactants or block-co-polymers as structure directing units

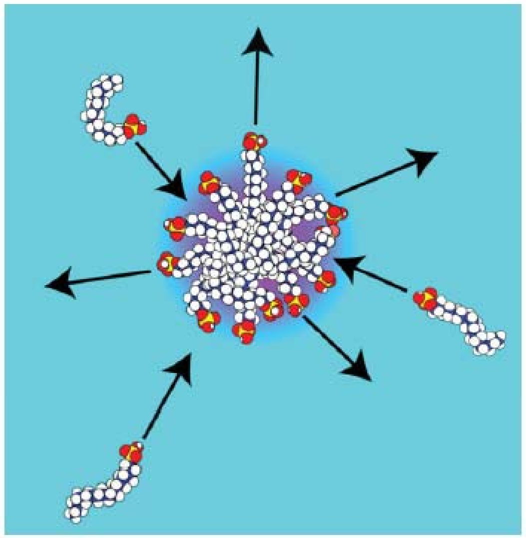


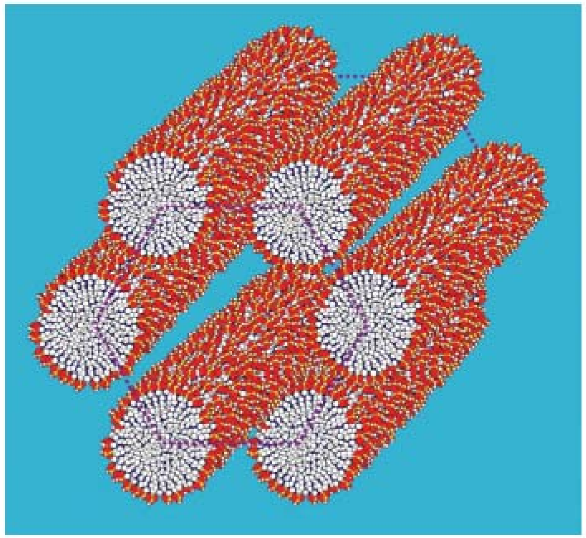
In aqeuous solutions amphiphilic surfactants or block-co-polymers form micelles;

with increasing surfactant concentration: spherical micelles ⇒ rod-like micelles ⇒arrangement of micelles.

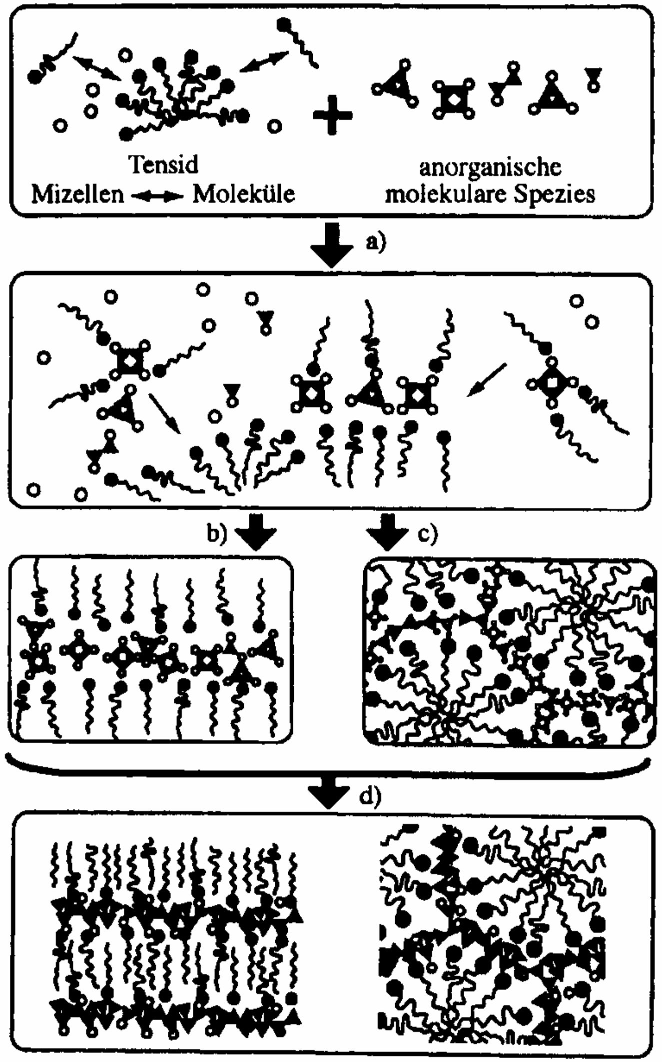
On the surface of the micelles the oxide monomers and oligomers can be arranged and condensate







Mechanism of formation

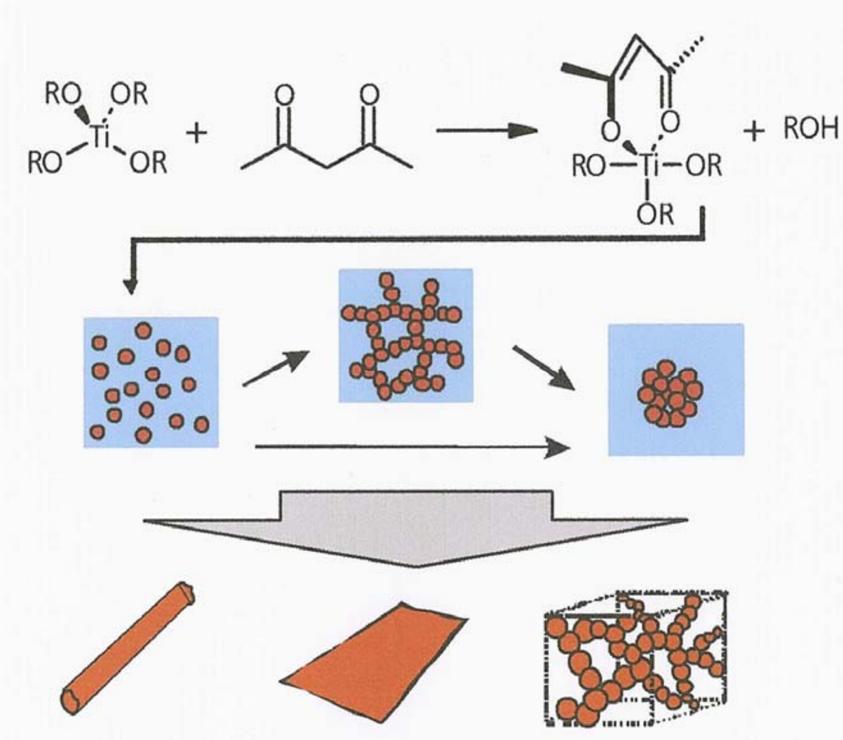


Cooperative effect between surfactants (partially micelles formed)

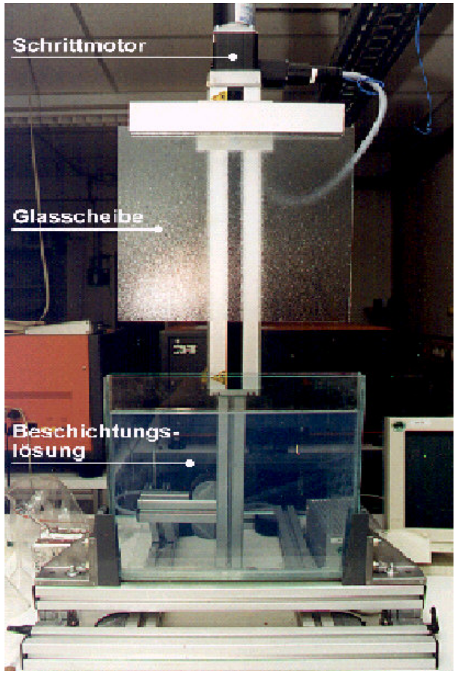
and

anionic silica (or titania) mono- or oligomers

Sol-gel-processing: formation of mesoporous SiO_2 or TiO_2 films



Dip-coating

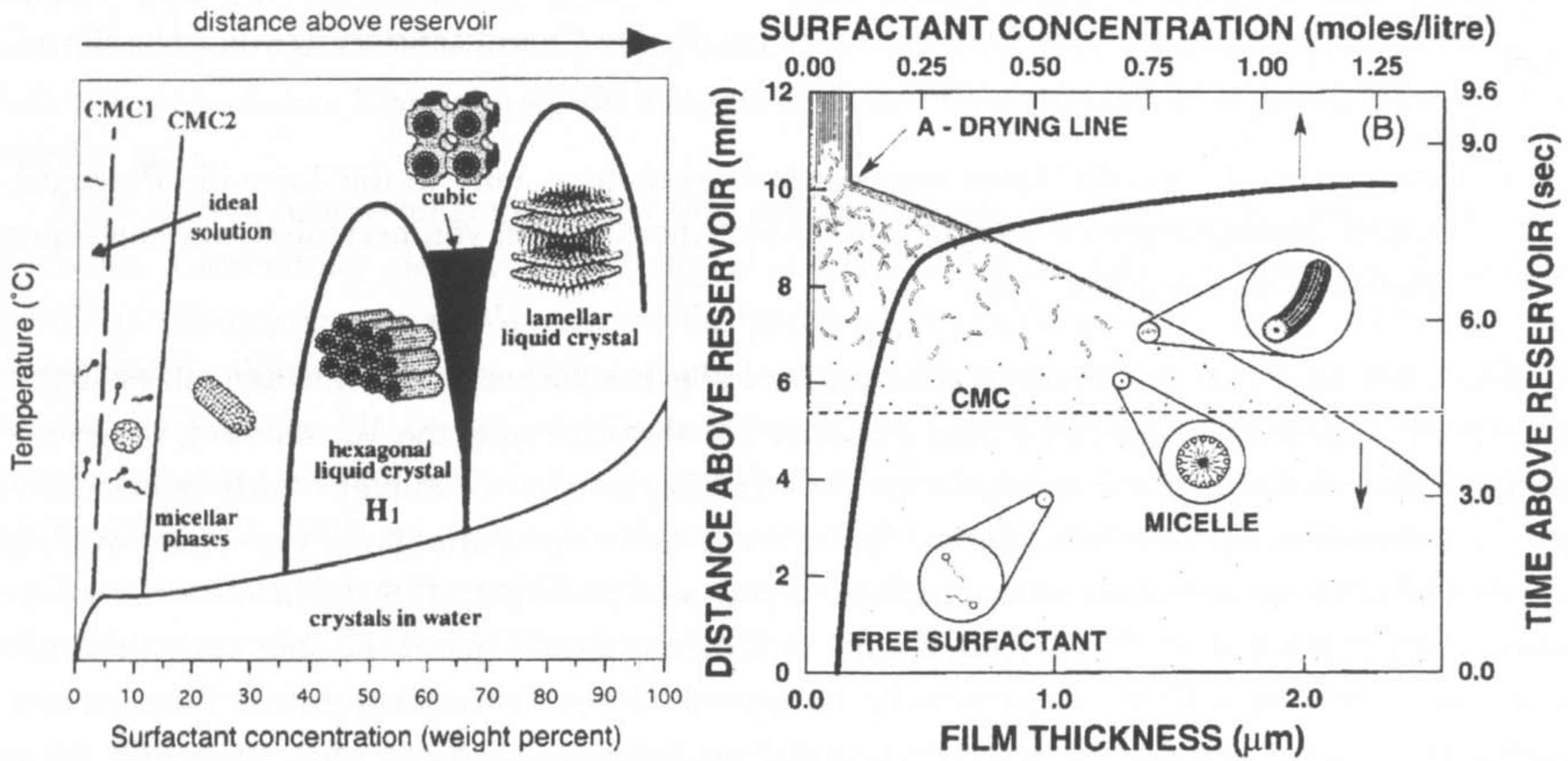


Transparent SiO_2 films:

- Dissolution of block-co-polymer P123 $(HO(CH_2CH_2O)_{20}[CH_2CH(CH_3)O]_{70}(CH_2CH_2O)_{20}H)$ addition of tetraethylorthosilicate (TEOS), 5 min stirring, ageing for 20 h at 35°C.
- Deposition on e.g. glass slides by dip-coating (withdrawal rate: 1 mm s^{-1}) at 25°C. *(⇒ EISA process)*
- Calcination at 350°C for 2 h (heating rate: 1°C min^{-1}).

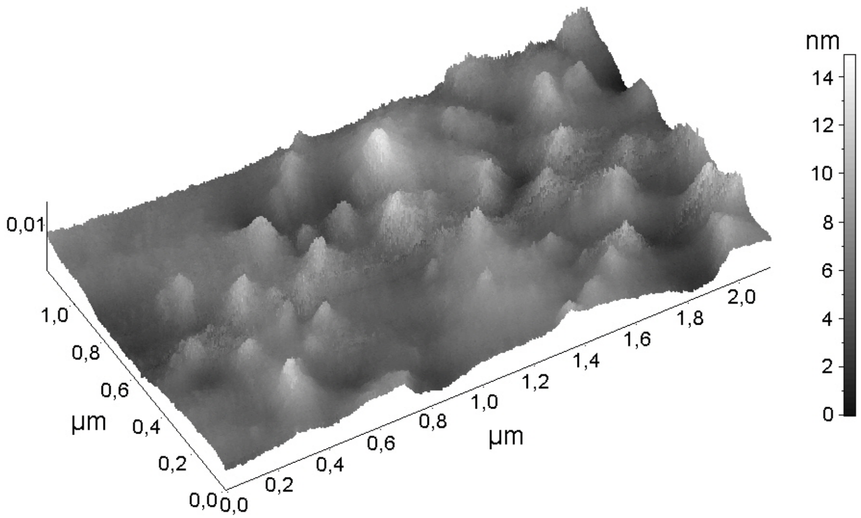
EISA process

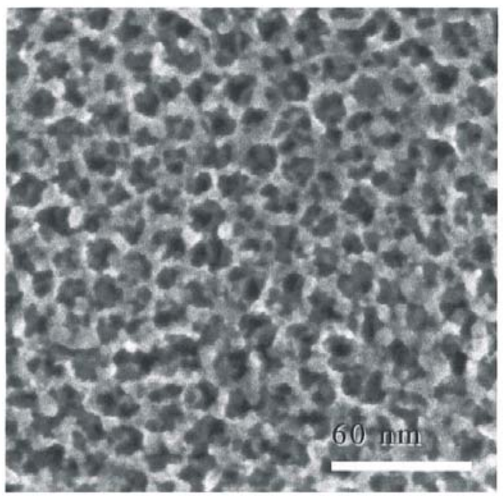
EISA: evaporation induced self-assembly



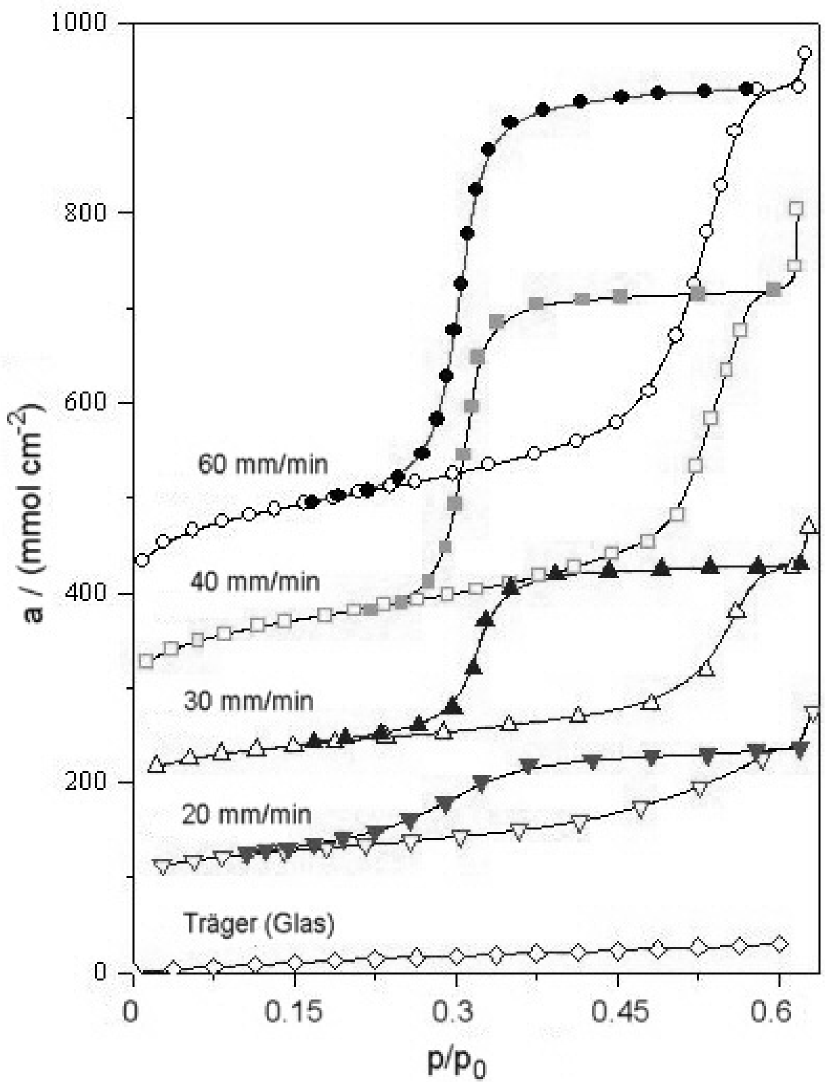
D. Zhao, G. Stucky et al. Adv. Mater. 10 (1998), 1380.

Mesoporous SiO_2 films on glass



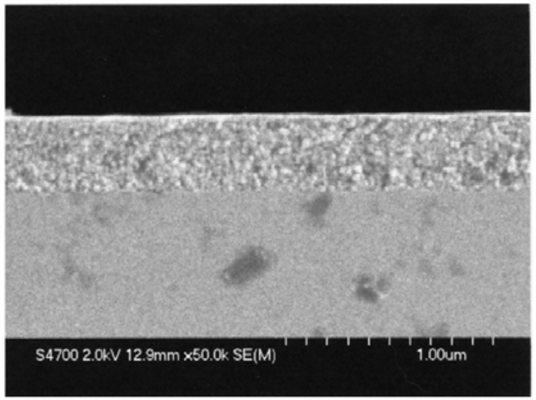


- Thickness: 200 – 400 nm.
- Roughness of the surface is low, around ± 7 nm (AFM).
- SEM: relatively regular pores (confirmed by Kr isotherms).

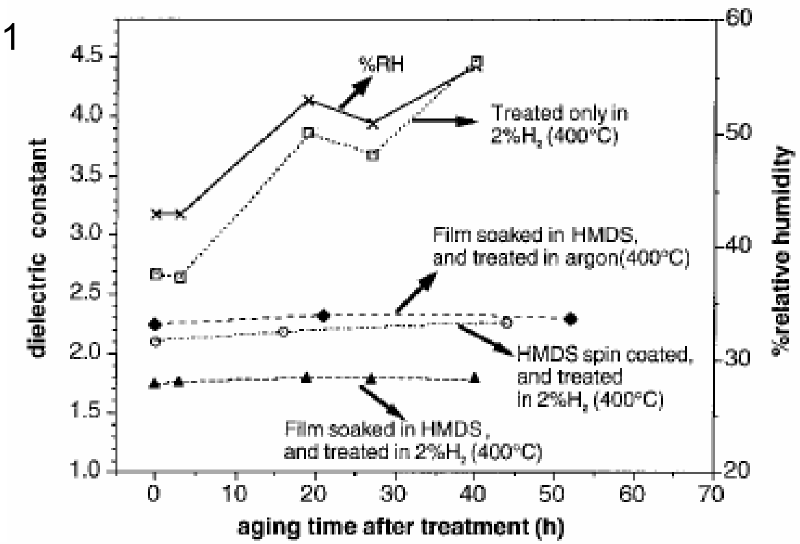


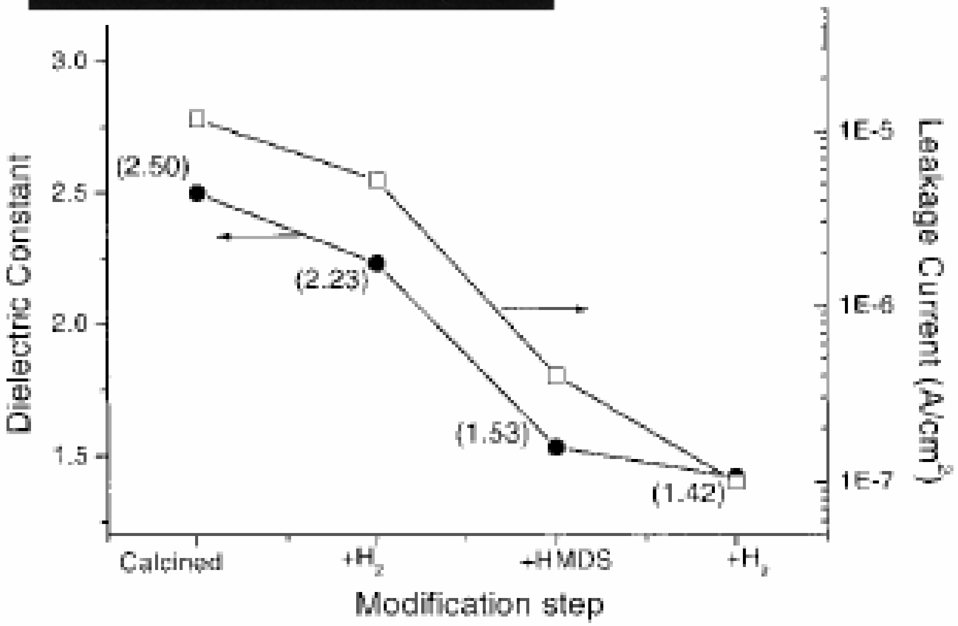
Mesoporous SiO_2 films as low-k materials

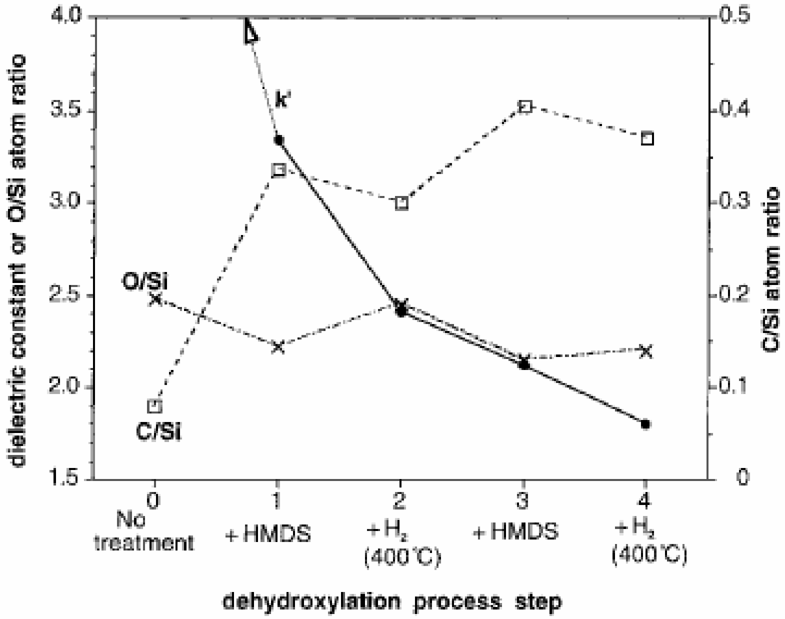
S. Baskaran, G.E. Fryxell et al. Adv. Mater. 12 (2000), 291
bzw. K.J. Chao et al., Adv. Mater. 13 (2001), 1099.



H_2 treatment and hydrophobization necessary to prevent formation of OH groups at the inner surface.



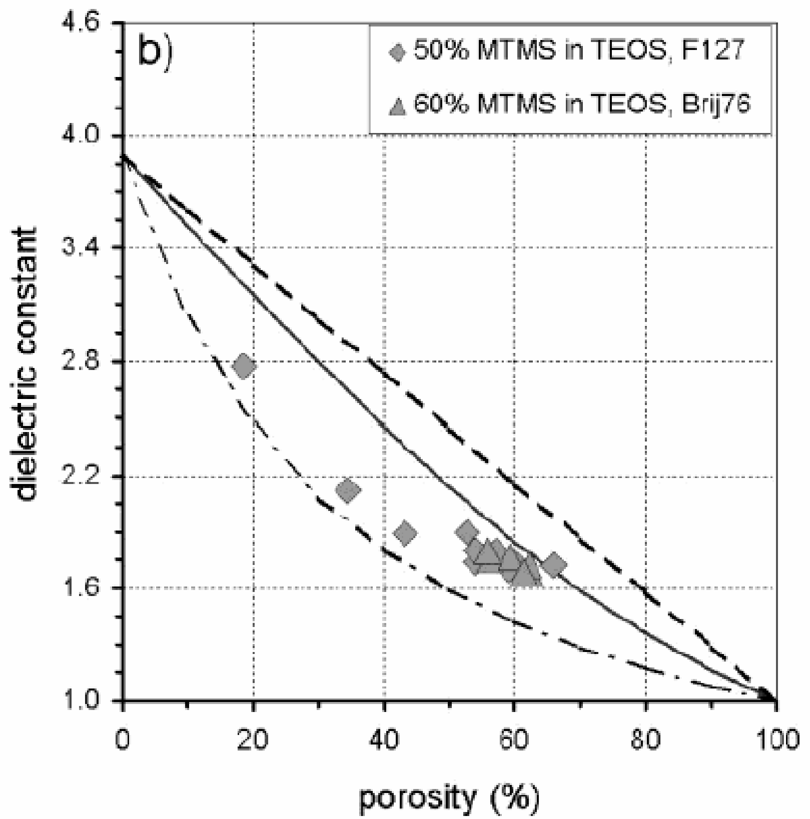




Mesoporous SiO_2 films as low-k materials

F.K. de Theije (Philips) et al., J. Phys. Chem. 107 (2003), 4280

Influence of porosity on dielectric constant and structuring



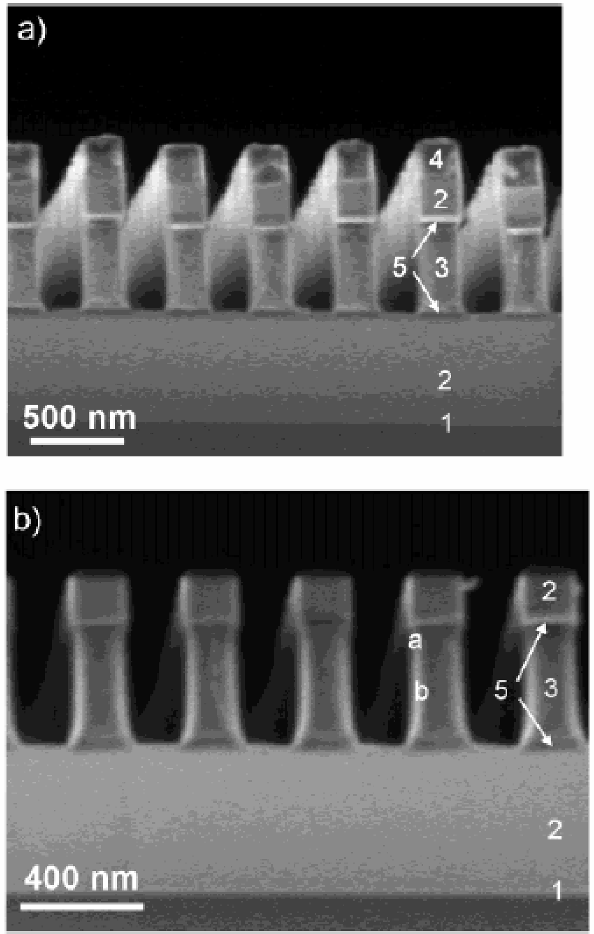


Figure 11. (a) Low-*k* stack after etching. (b) Same stack after resist stripping in O_2/N_2. Trenches are 200 nm wide. (1) Si_3N_4, (2) SiO_2, (3) low-*k*, (4) photoresist, and (5) SiC. The trenches show some undercutting (a) and bowing (b).

Mesoporous SiO_2 films as low-k materials

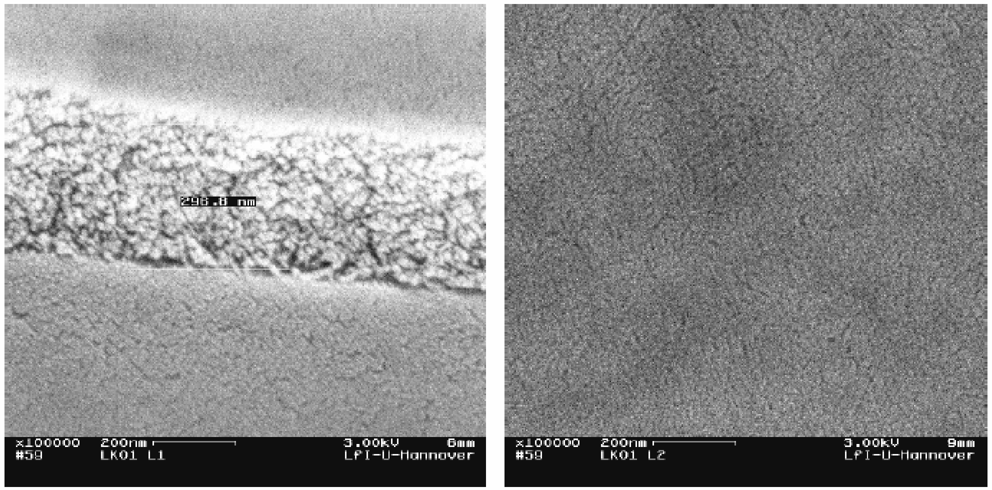
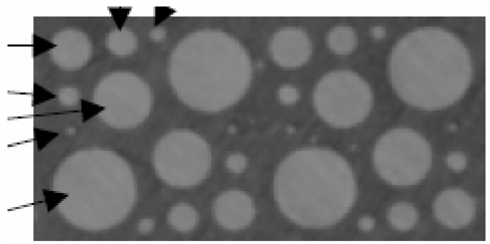


Abb.1 a) Querschnitt b) Draufsicht

Own results (with M. Czernohorsky, H.J. Osten)

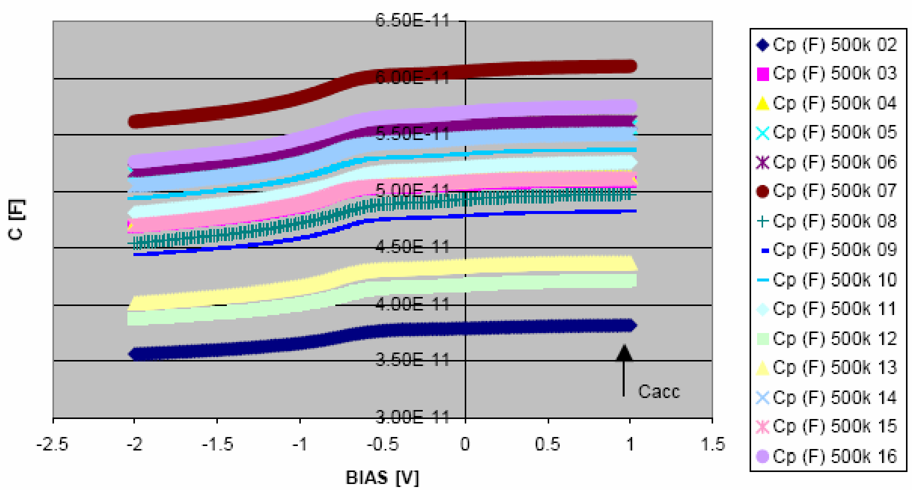


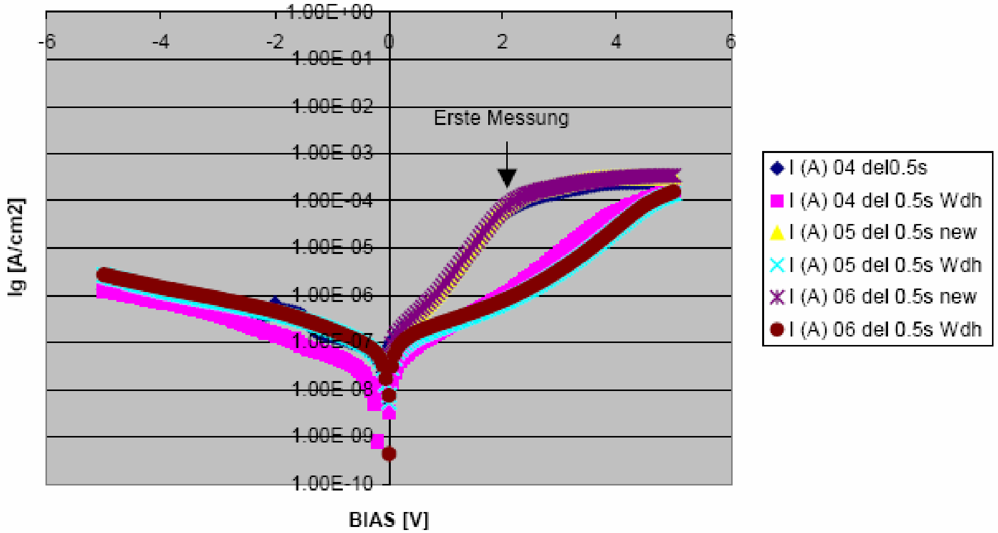
Lochmaske für Metall-Dots

Mesoporous SiO_2 on Si substrate

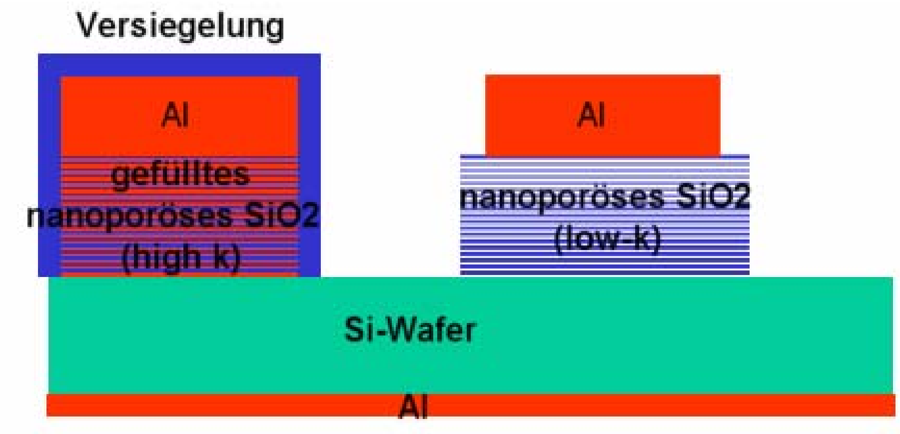
Sputtern with Al contact

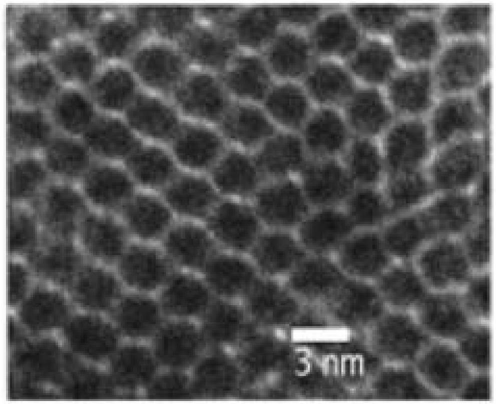
ε value of about 14 ⇒ too high, effective layer thickness less than 300 nm, Al diffuses into porous SiO_2





Filling the pores of mesoporous oxide films





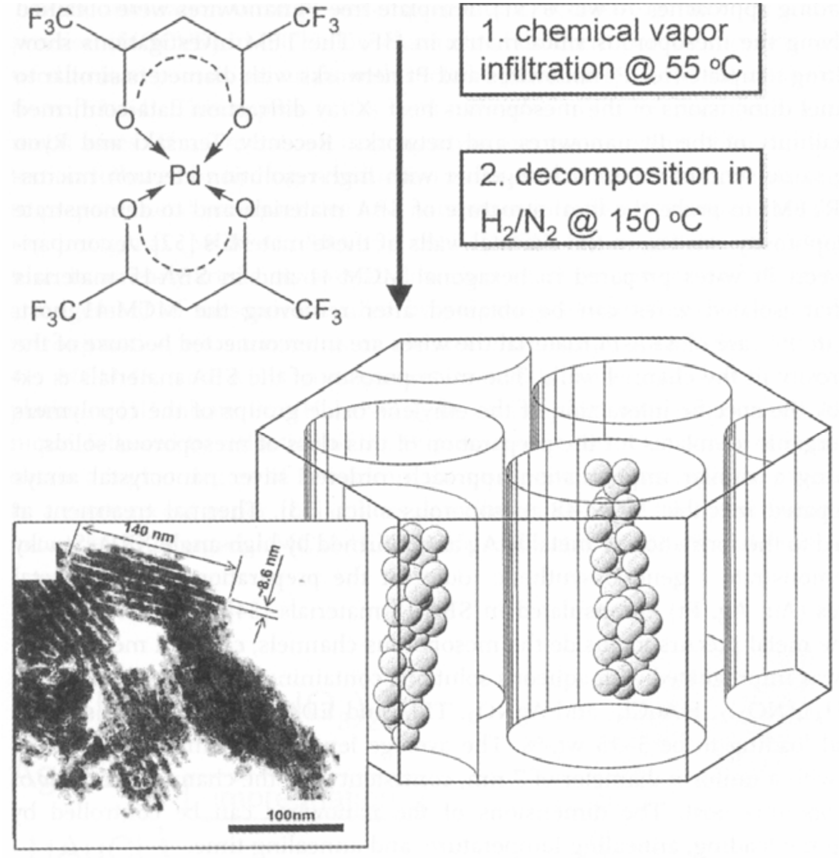
Idea: Different layers on a chip: insulating (low-k layer), conducting (hig-k layer)

Easiest method for filling of the pores:
adsorption from gas phase
but chemical coupling to wall necessary

Filling the pores of mesoporous oxide films

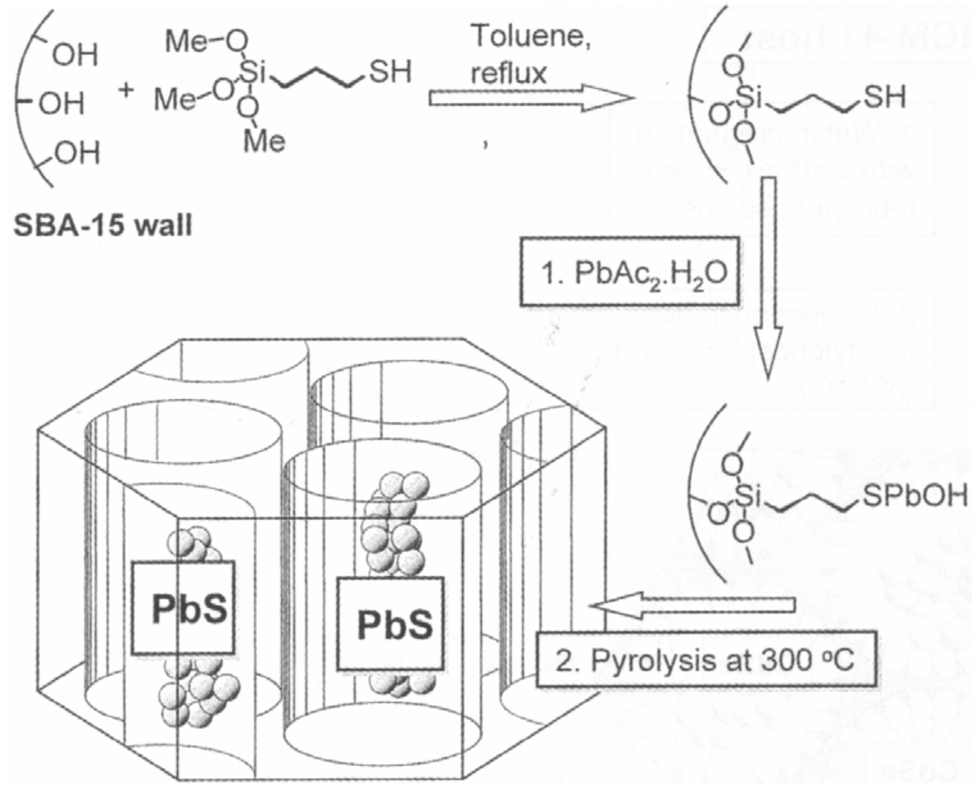
Pd nanowires in mesoporous SiO_2 (SBA-15)

H. Kang et al., Chem. Mater. 12 (2000), 3530



PbS nanowires in mesoporous SiO_2 (SBA-15)

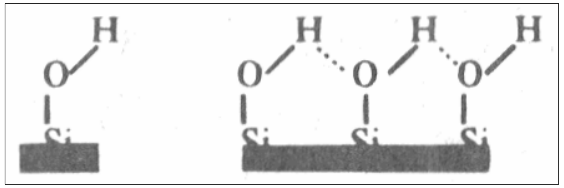
F. Gao et al., Nano Letters 12 (2001), 743



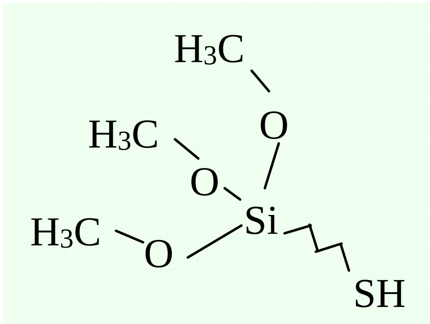
CdS nanoparticles in mesoporous SiO_2 powders (M-41S)

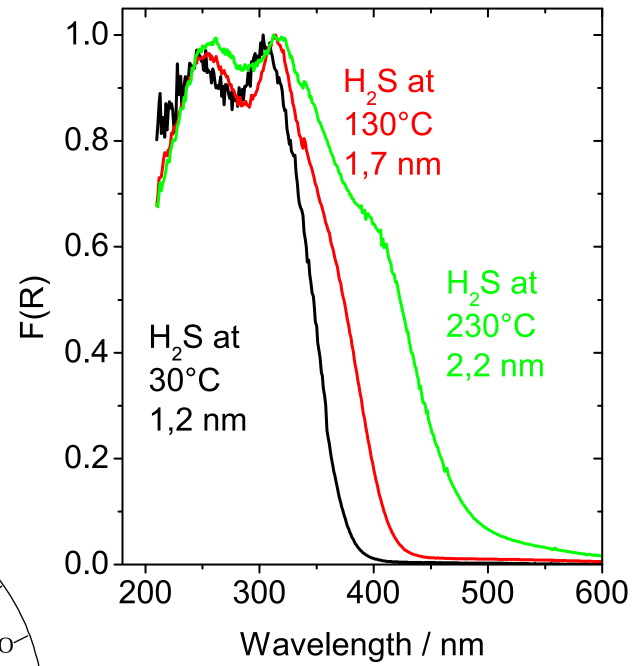
1. Step: Modification of the inner surface of SiO_2-M41S

Isolated and bridged silanol groups



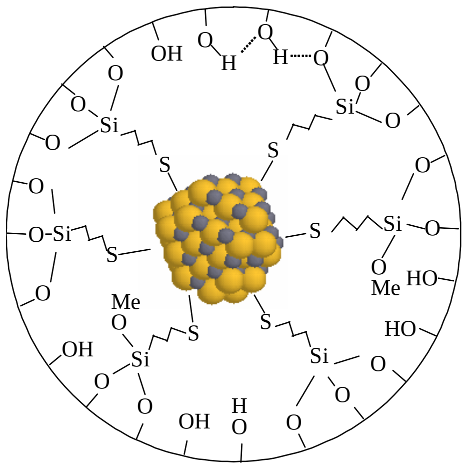
thiols as anchors





2. Step: Impregnation with Cd^{2+} ions;

3. Step: Reaction with H_2S from gas phase.



⇒ At low temperatures, the growth is determined by the mobility of the Cd^{2+} ions

H. Wellmann, M. Wark et al., Microp. Mesop. Mater., 44-45 (2001), 419.

Formation of CdS or CdSe nanoparticles in the films

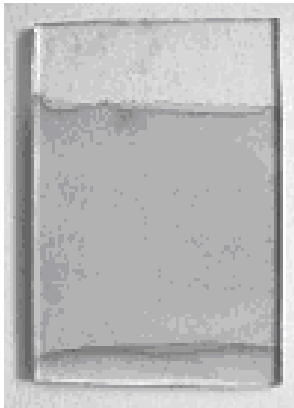
Two different routes are possible:

- Impregnation or dip-coating of the films with aqueous $CdAc_2$
  $\Rightarrow$ inhomogeneous distribution of CdS/CdSe particles (after treatment with H_2Se, even at low loadings)
- Bulk-CdSe is formed.

- Addition of $CdAc_2$ directly during the synthesis of the films
  $\Rightarrow$ homogeneous distribution of the Cd^{2+} ions
  $\Rightarrow$ homogeneously colored films
- Formation of 2-3 nm CdSe particles

impregnation

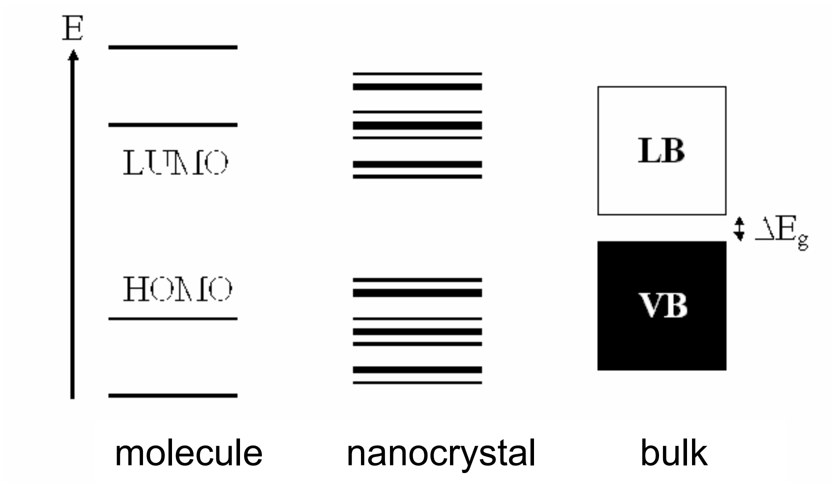
dip-coating

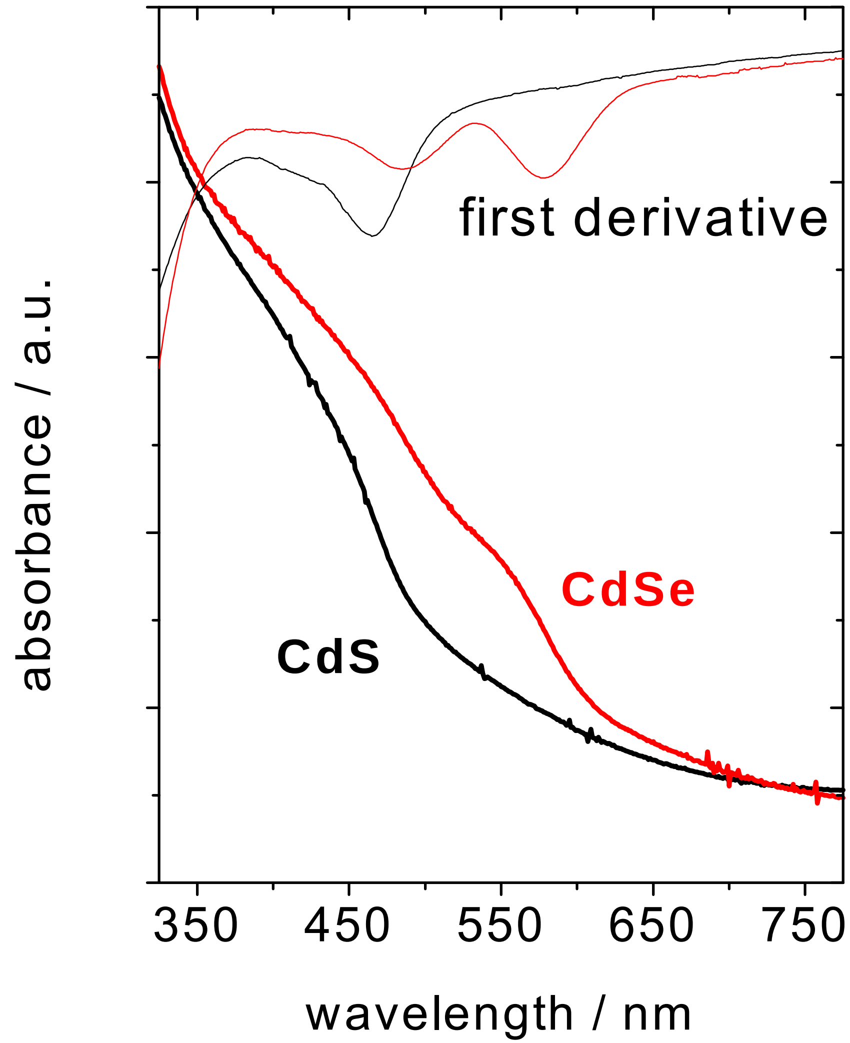


Direct addition of $CdAc_2$ to the synthesis gel (template solution)

UV/vis spectra of CdSe loaded mesoporous SiO_2 films

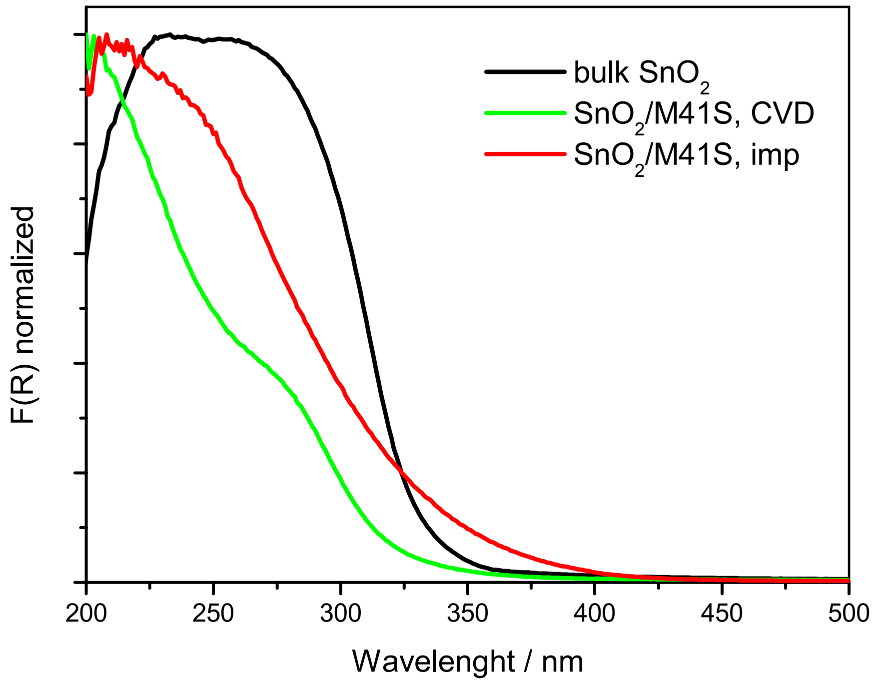
- The films contain nanometer-sized CdS and CdSe particles.
- As deduced from the structured first derivatives of the absorption spectra (quantum size effects), most particles possess diameters of 2-3 nm.

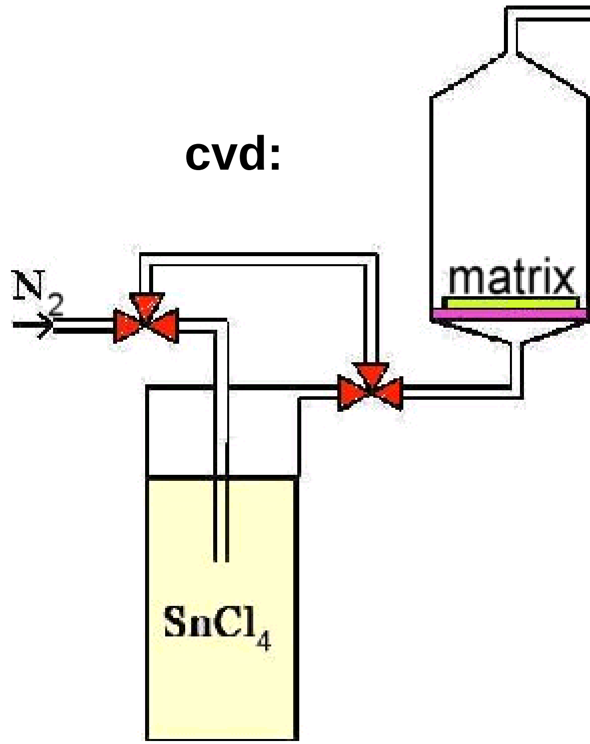


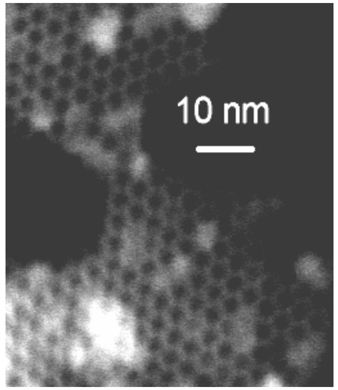


SnO_2 nanoparticles in mesoporous oxides

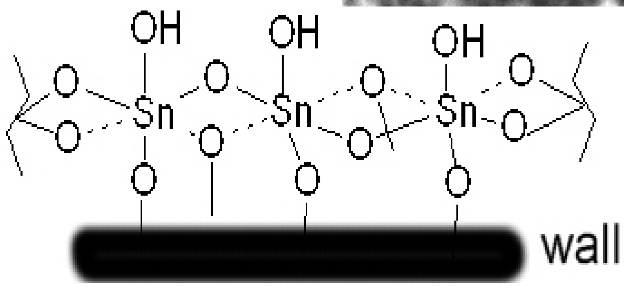
Diffuse reflectance UV/Vis spectra





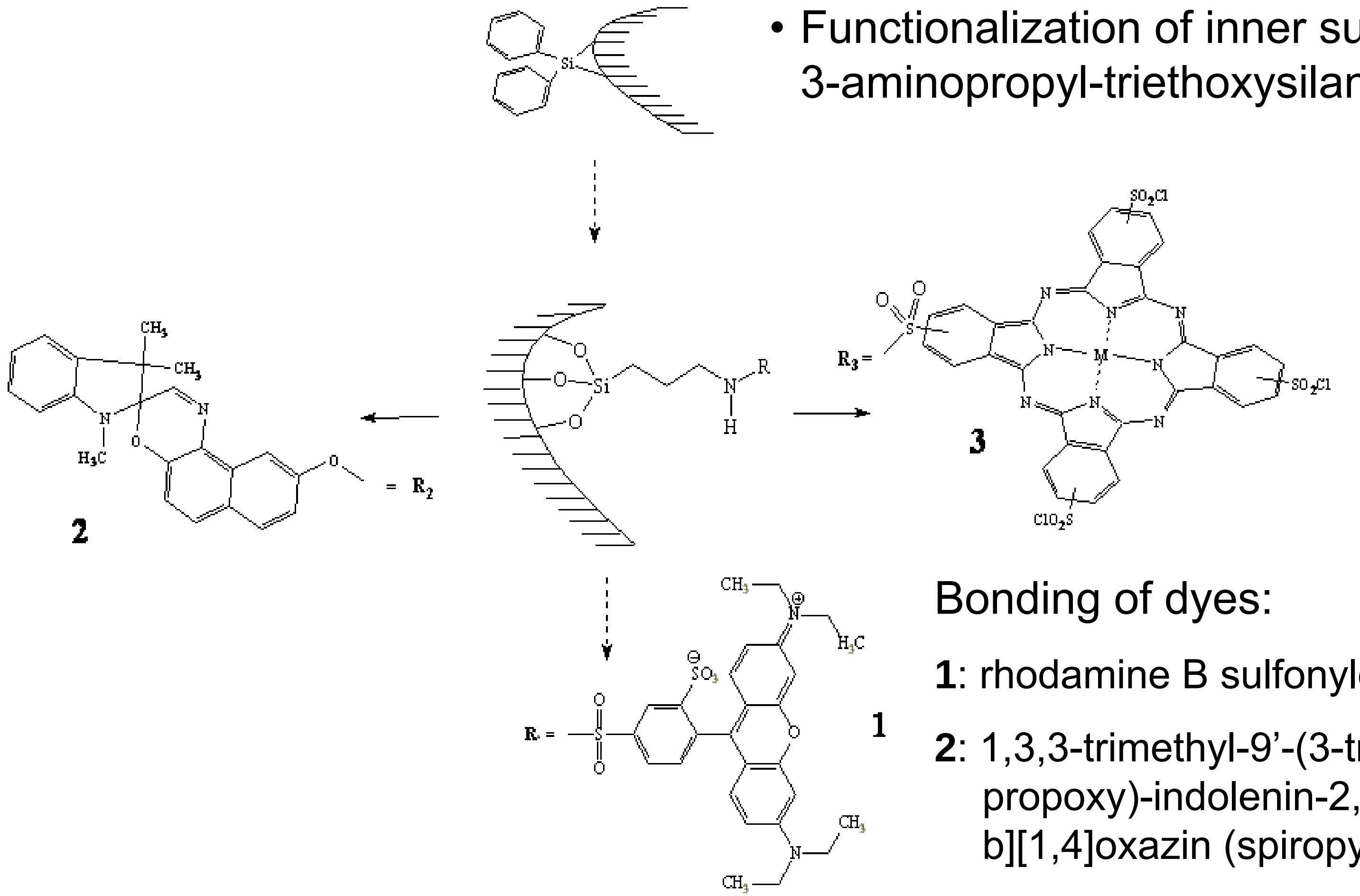


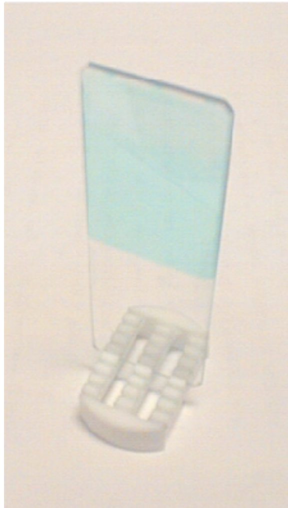
- Smallest particles < 2 nm in Si-MCM-41 (most pronounced blue-shift of the absorption edge)
- 2-dimensional layer of SnO_2 forms on the inner pore walls of the nanoporous SiO_2-M41S material



Concept of modification of silica thin films with dyes

- Pre-silylation with diphenyldichlorosilane
- Functionalization of inner surface with 3-aminopropyl-triethoxysilane





Bonding of dyes:

1: rhodamine B sulfonylchloride

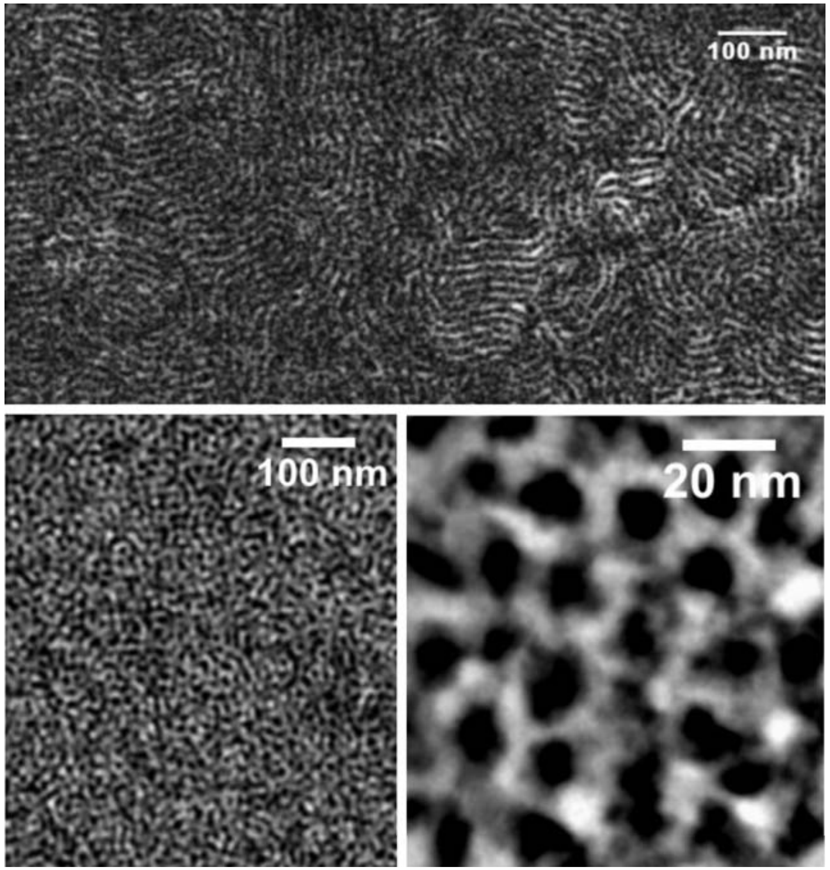
2: 1,3,3-trimethyl-9'-(3-trimethoxysilyl-propoxy)-indolenin-2,3'-[3*H*]naphth[2,1-b][1,4]oxazin (spiropyran dye)

3: metal phthalocyanine tetrasulfonylchloride (PTS)

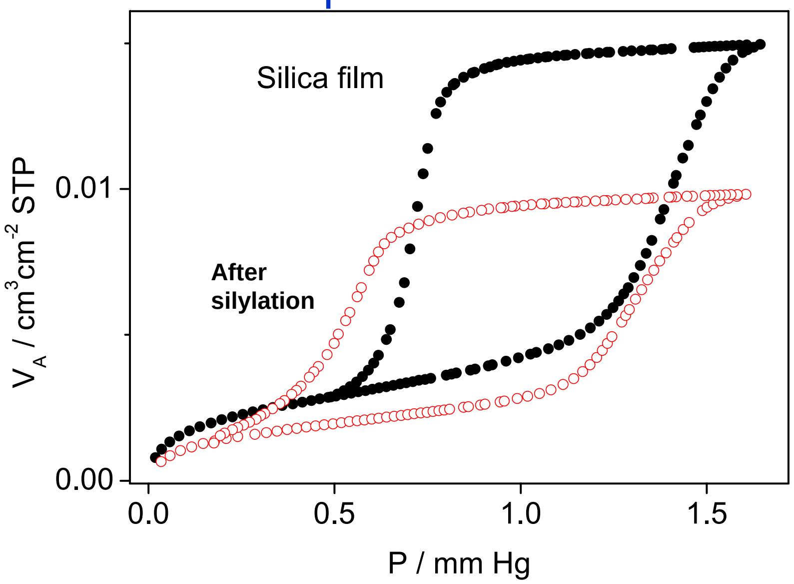
Y. Rohlfing, M. Wark et al.,
Stud. Surf. Sci. Catal. 142 (2002), 1067

Mesoporous SiO_2 films: texture, accessibility of inner volume

SEM, TEM



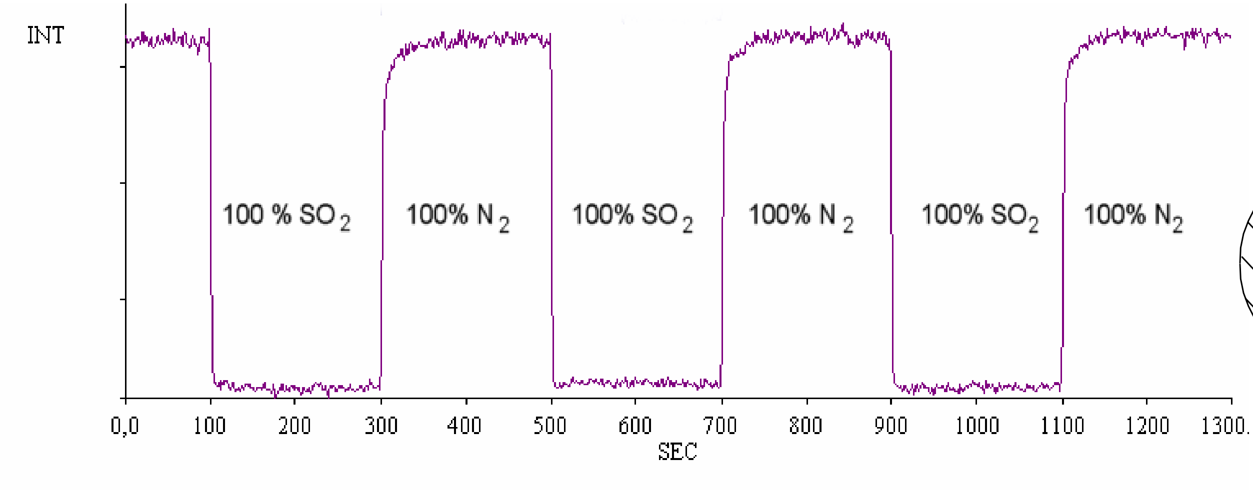
Kr adsorption

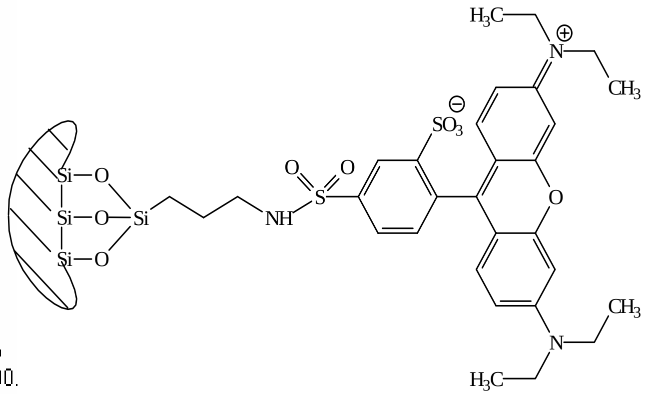


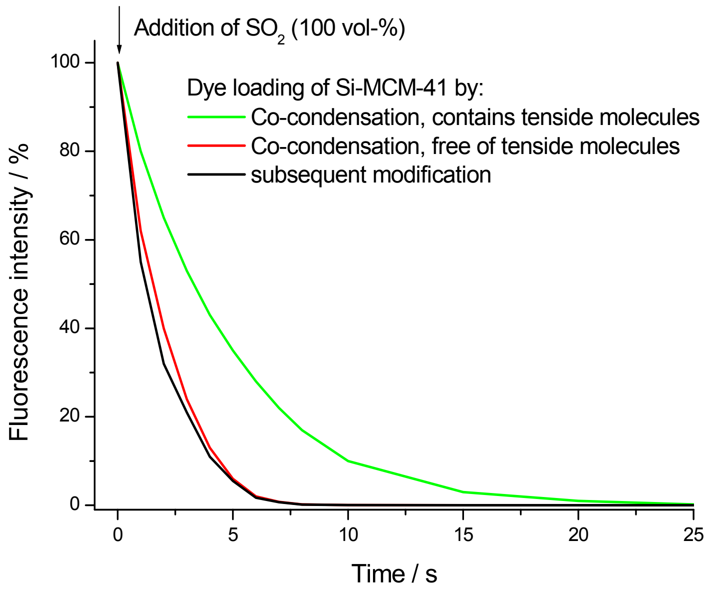
Silica film	Roughness factor	Porosity	Pore diameter
Pristine	**122**	**60%**	**6.85 nm**
After silylation	**82**	**40 %**	**6.27 nm**

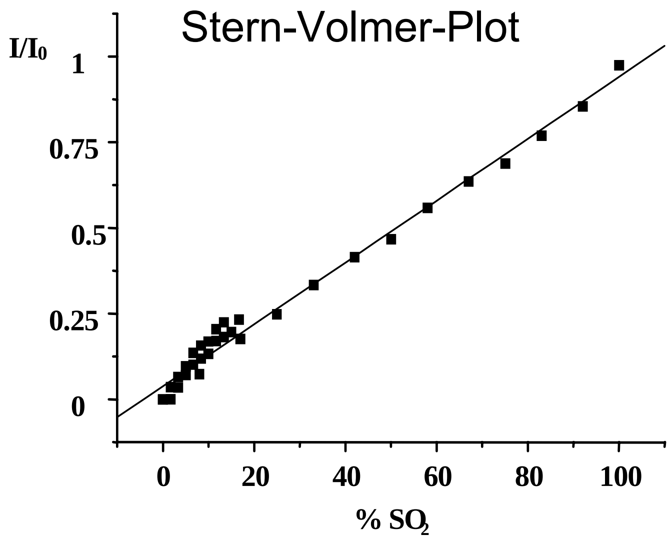
Surface accessibility: 70-75%
(electrochemical probe)

Application as fluorescence sensing system for SO_2

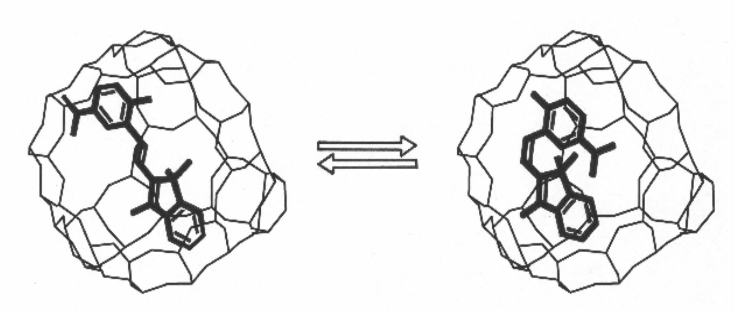


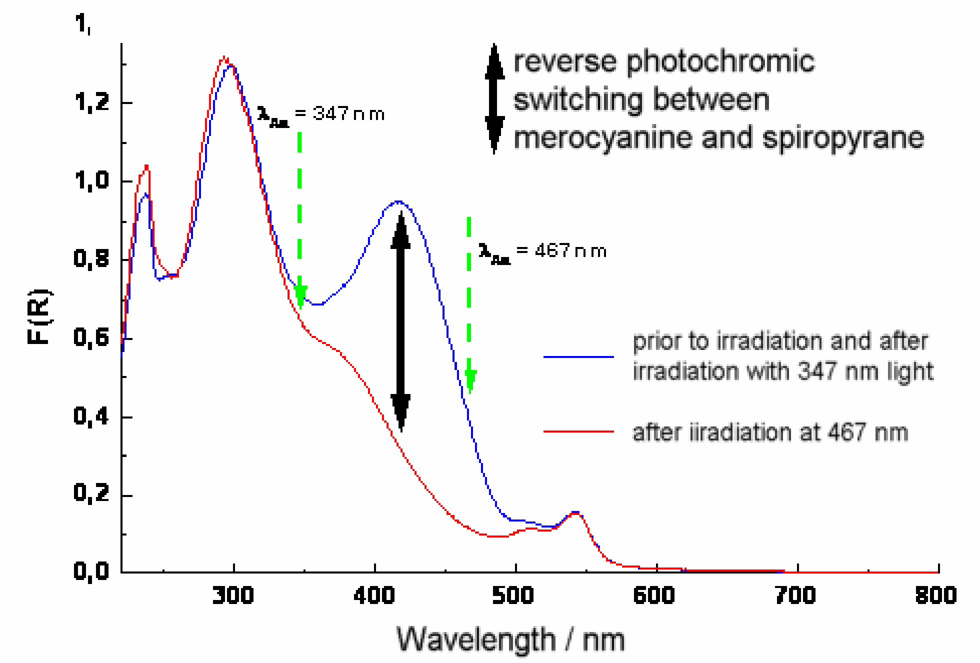


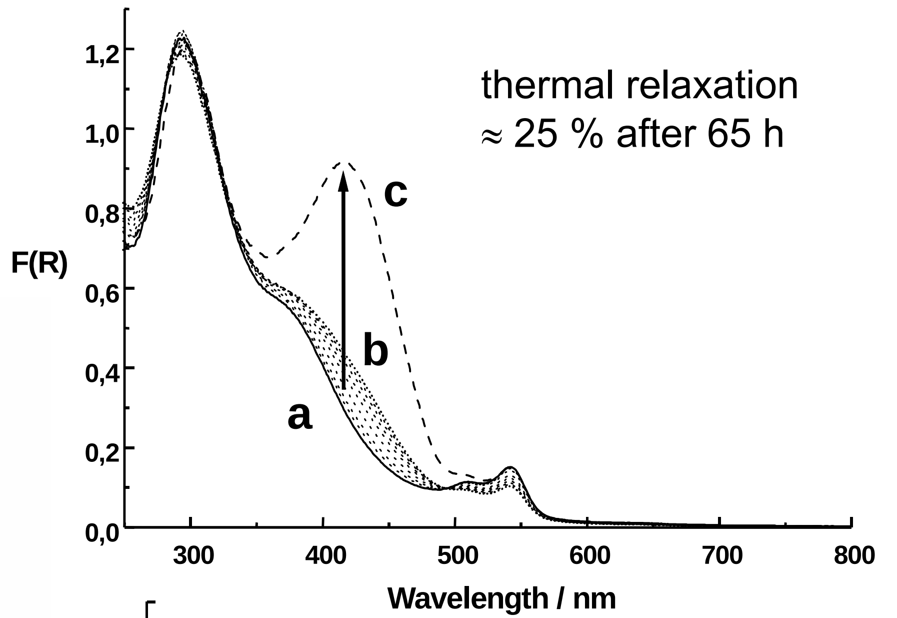


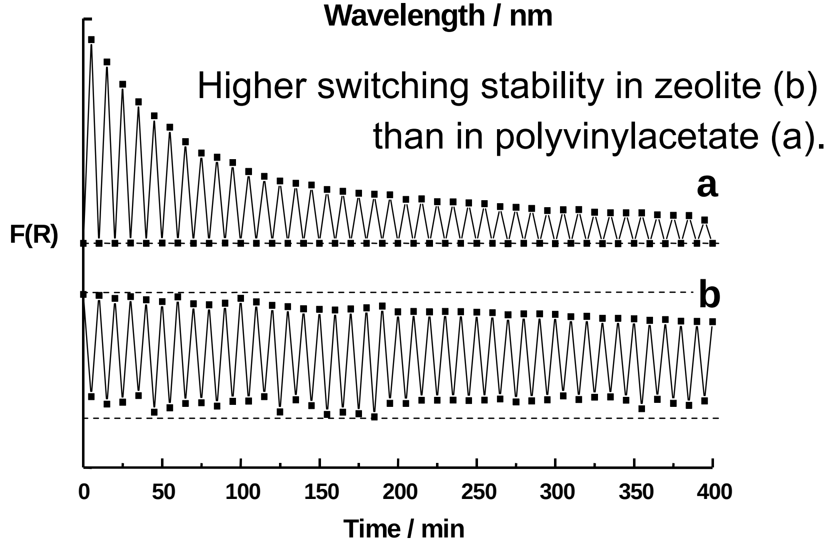


Optical switches: spiropyrans in the pores of zeolite Y







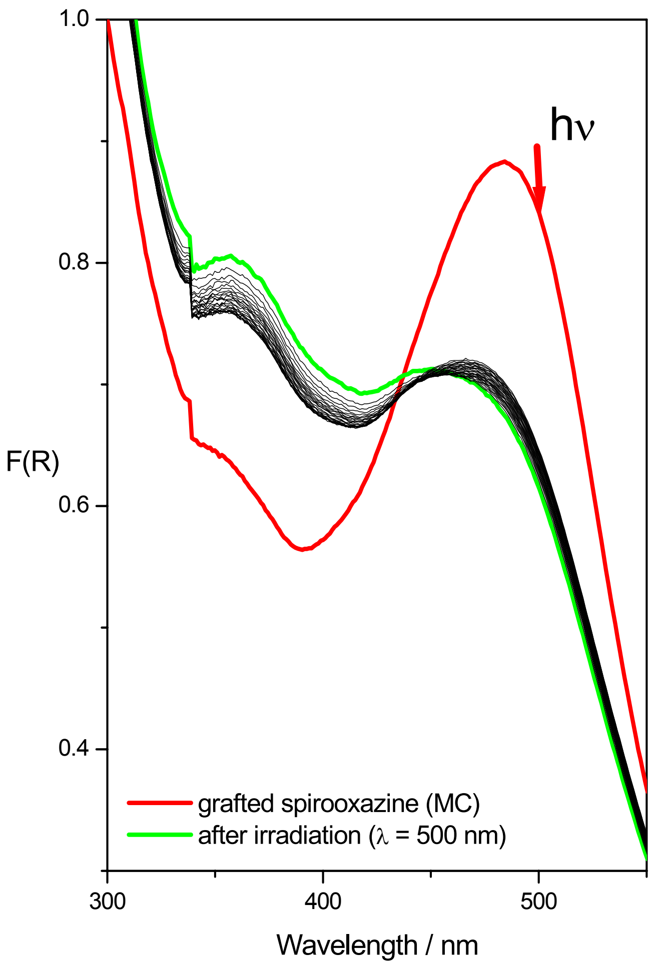


C. Schomburg, M. Wark et al., J. Mater. Chem. 11 (2001) 2014.

Switching of spirooxazine anchored in mesoporous oxides

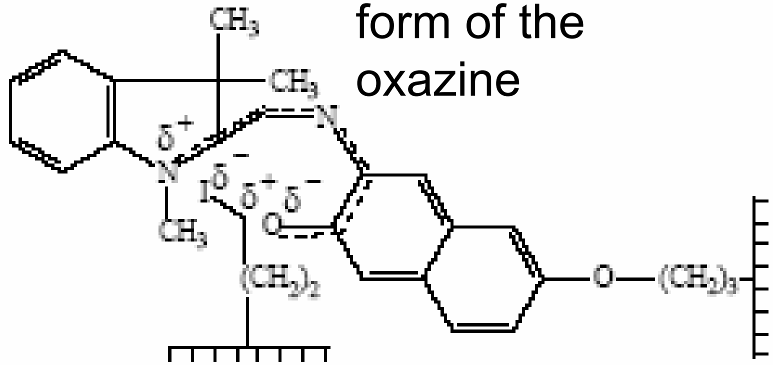
Switching in mesoporous hosts (larger pores, no sterical hindrance

(from photomerocyanine to new cis-cisoid form)



- Again no complete thermal relaxation after 50 h (only ≈ 20 %)
- Reverse switching with 350 nm light.

Jodo-function on SiO_2 surface (introduced for the functionalization) stabilises open cis-cisoid-form of the oxazine



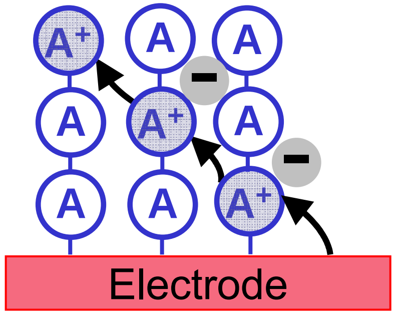
Immobilization of discrete electroactive species in SiO_2 films

Propagation mechanism:

-Electron transfer **from** electrode:

heterogeneous + homogeneous (hopping)

-Ion transfer **to** electrode (charge balance)

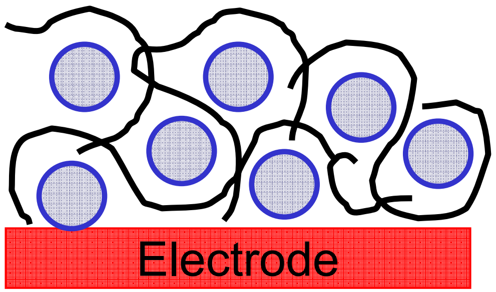


Self-assembled electrodes

or

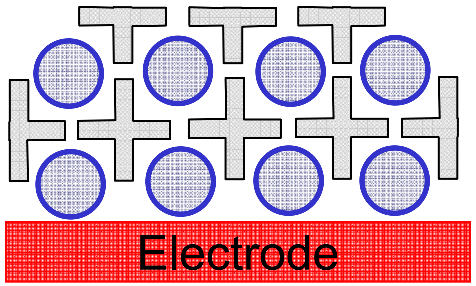
Supported electrodes

Organic matrix



-Non-universal
-Non-defined texture
-Low stability in organic solvents

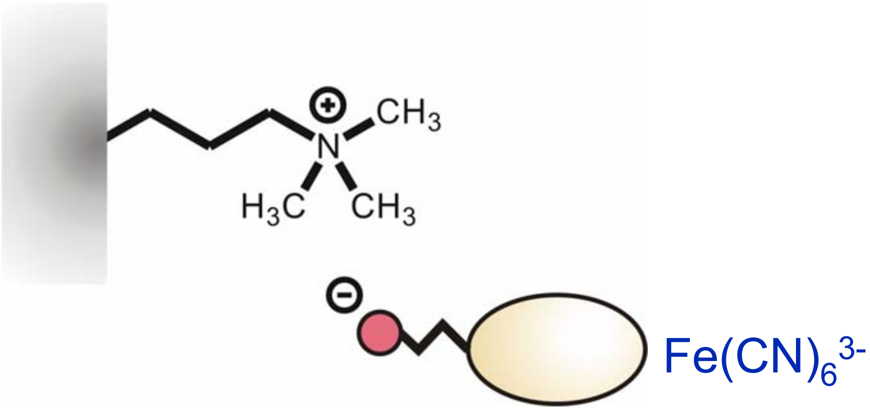
Inorganic matrix



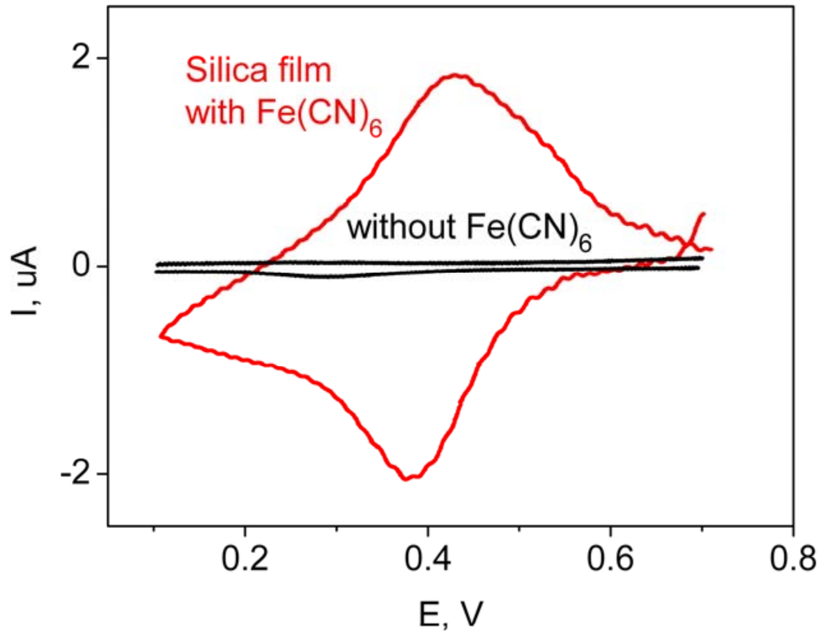
Advantages:
-Robust
-High mechanical stability
-Films of controllable thickness

Mesoporous SiO_2 films: immobilization of $[Fe(CN)_6]^{3-}$ ions

Ionic immobilization



Hexacyanoferrate in silica film



Concentration of $Fe(CN)_6$ in silica film:

$1.1\cdot10^{-8}$ mol cm^{-2} (ca. 260 μmol cm^{-3})

monolayer: $2 \cdot 10^{-11}$ mol cm^{-2}

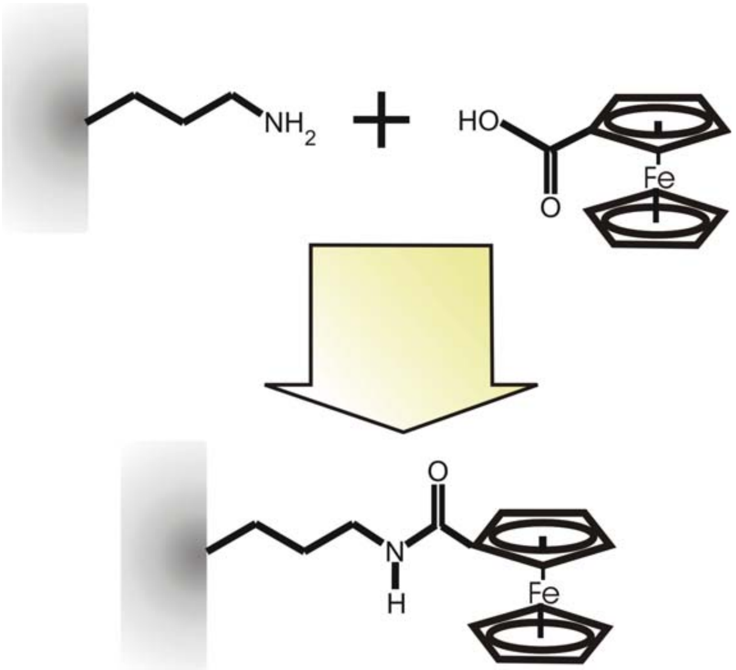
Charge uptake: dependence on film thickness

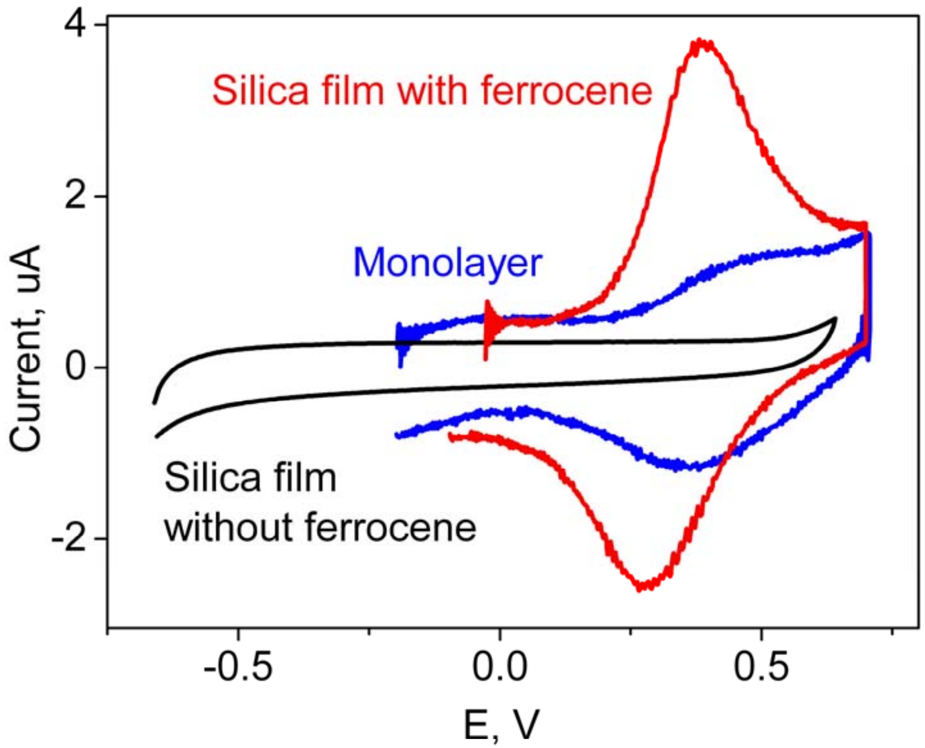
Film thickness ratio: 1.43
Charge uptake ratio: 1.55

D. Fattakhova, J. Rathousky, M. Wark, Langmuir, in press.

Silica films: covalent immobilization of ferrocene

Peptide bonding



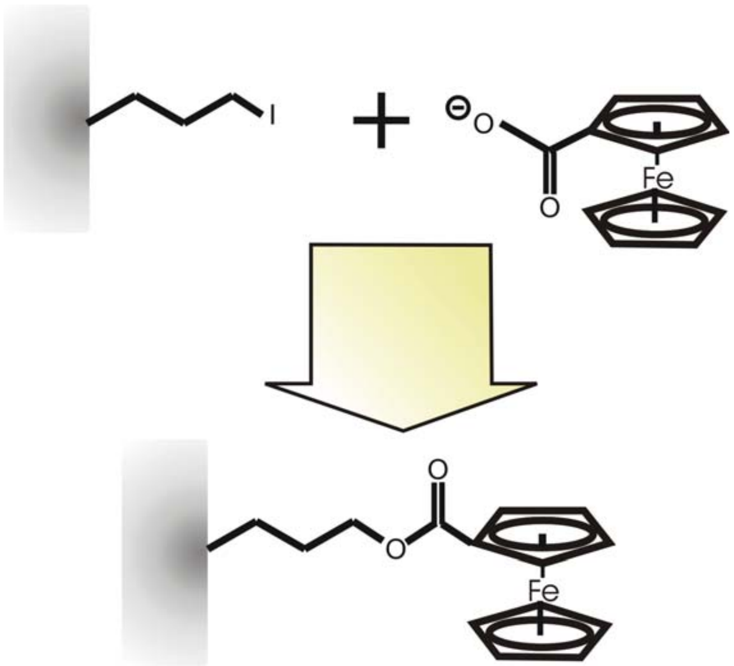


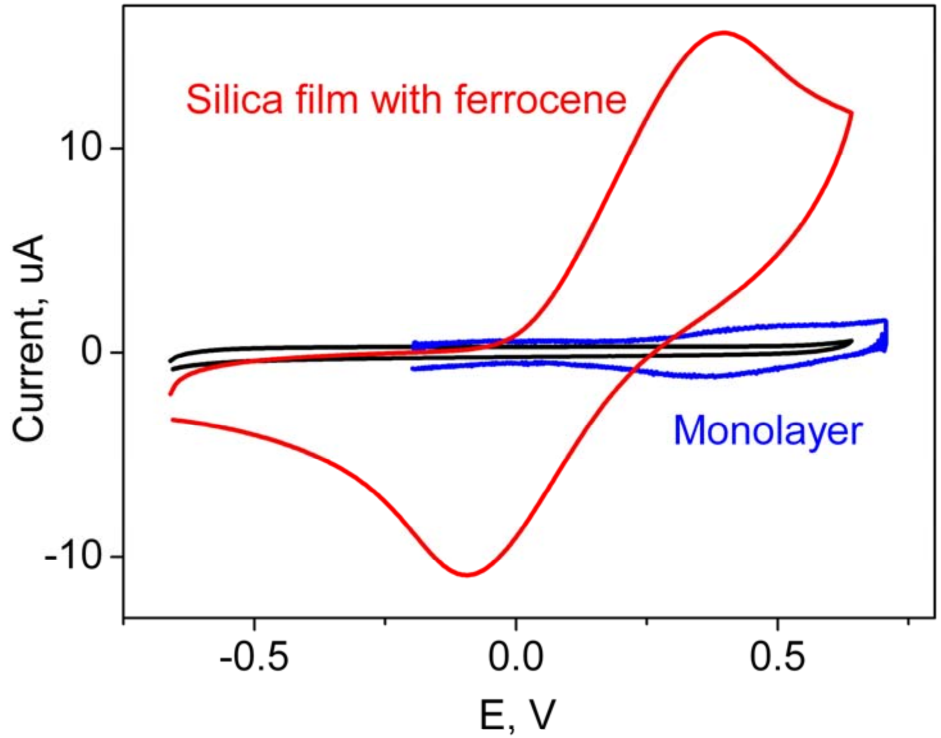
Surface coverage

Monolayer:	**$8.0 \cdot 10^{-11}$ mol cm^{-2}**
Silica (peptide):	**$3.2 \cdot 10^{-10}$ mol cm^{-2} (4 times)**

Silica films: covalent immobilization of ferrocene

Ester bonding





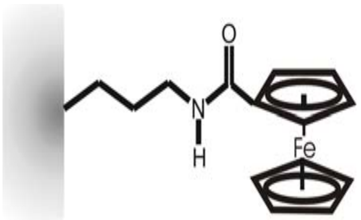
Concentration in film:
60 μmol cm^{-3} (voltammetry)

Surface coverage

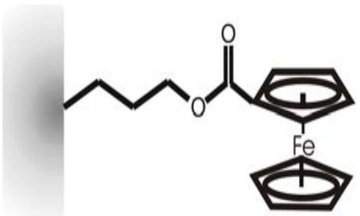
Monolayer:	**8.0 · 10^{-11} mol cm^{-2}**
Silica (peptide):	**3.2 · 10^{-10} mol cm^{-2} (4 times)**
Silica (ester):	**2.2 · 10^{-9} mol cm^{-2} (30 times)**

Silica films: covalent immobilization of ferrocene

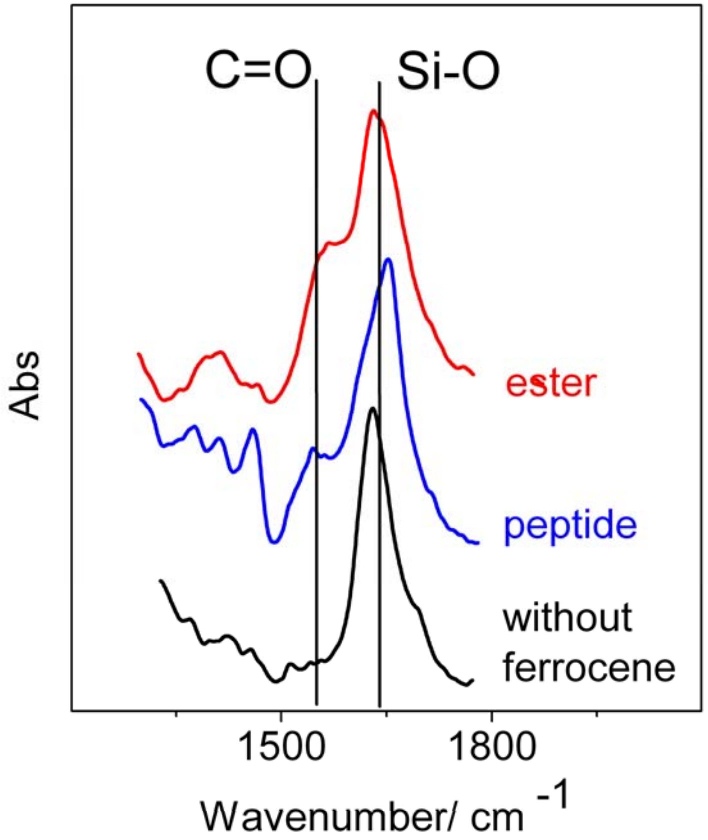
Peptide bonding



Ester bonding



FTIR ATR: efficiency of bonding

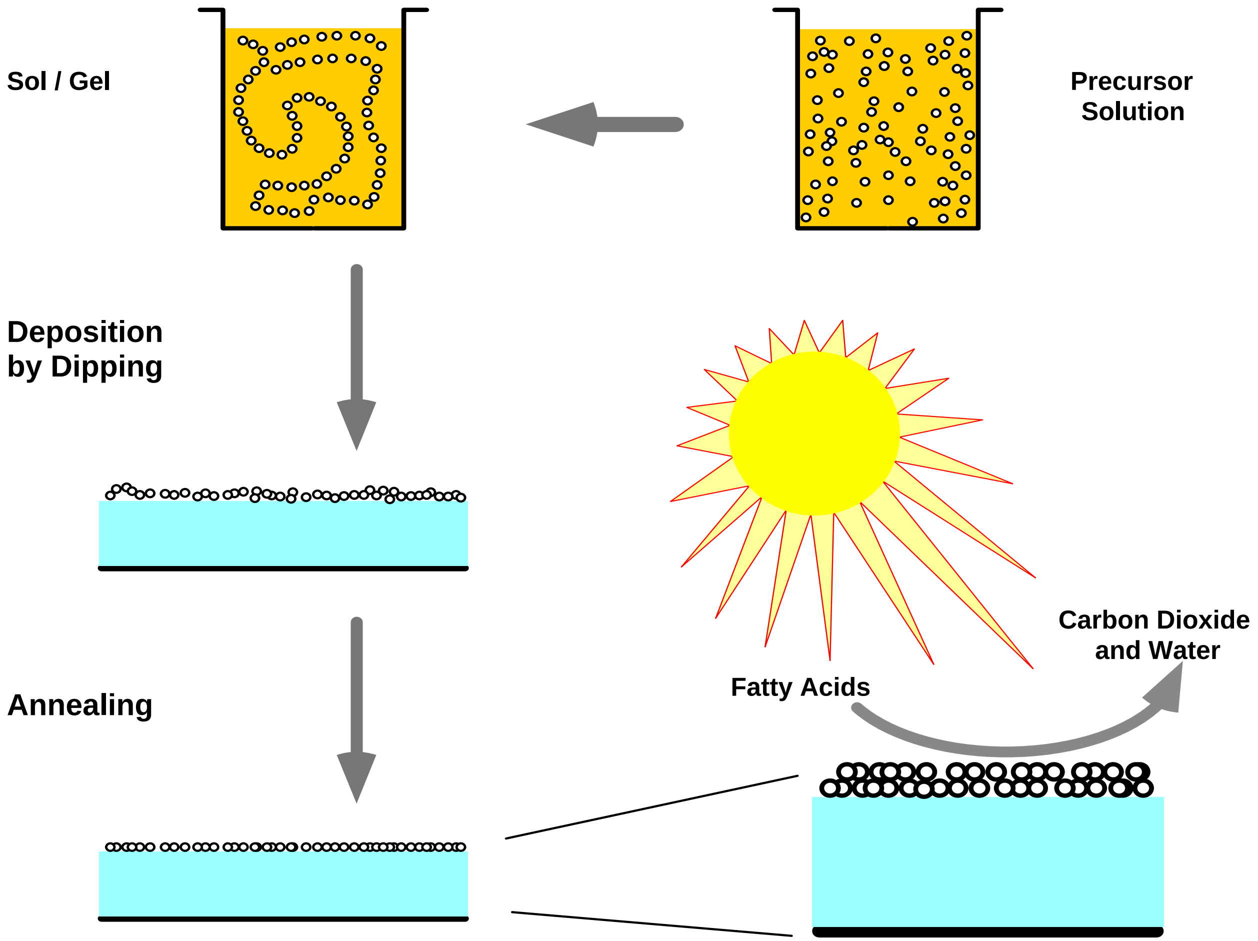


ν(C=O)
relative intensity:

0.6

0.3

Mesoporous TiO_2 films for photocatalysis



- $TiCl_4 + 2\ C_2H_5OH \rightarrow$ **$TiCl_2(OC_2H_5)_2$** $+ 2\ HCl$
  ⇧
  (relatively stable against hydrolysis)

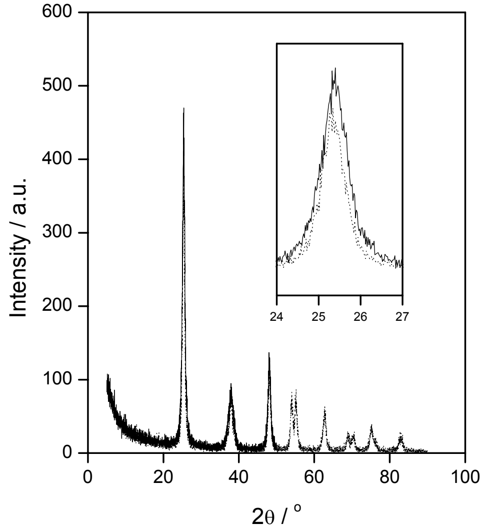
- **Block copolymer template (e.g. Pluronic P123)** to produce a **self-assembling complex**

- Air humidity causes slow hydrolysis of the titanium component.

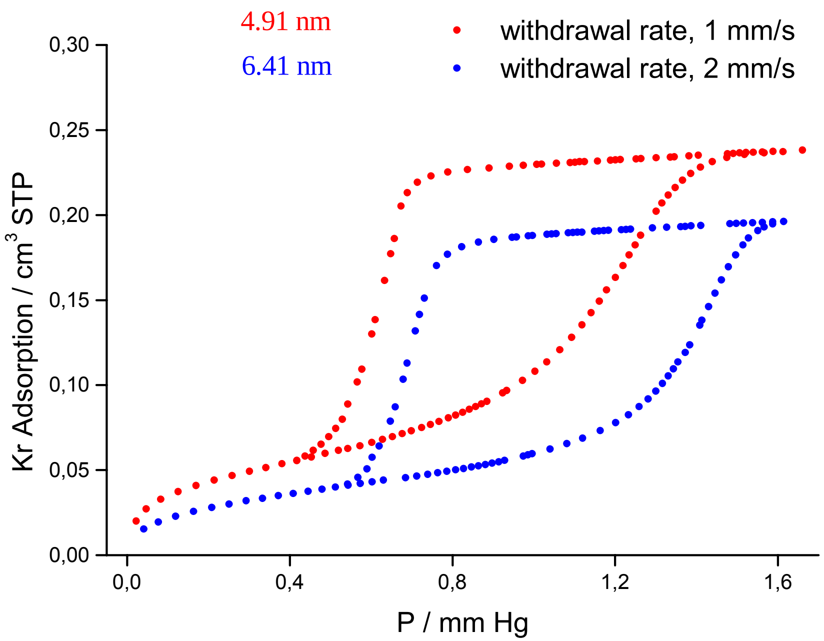
- Calcination in air removes quantitatively the organic template

Model of the structure of mesoporous titania film

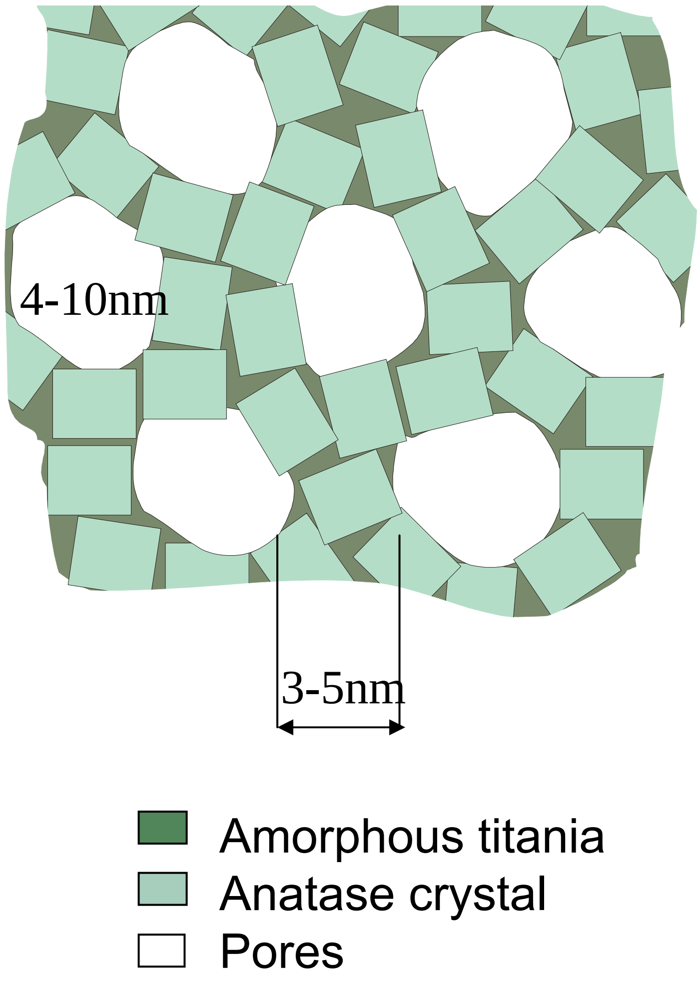
XRD ⇒ proves crystallinity



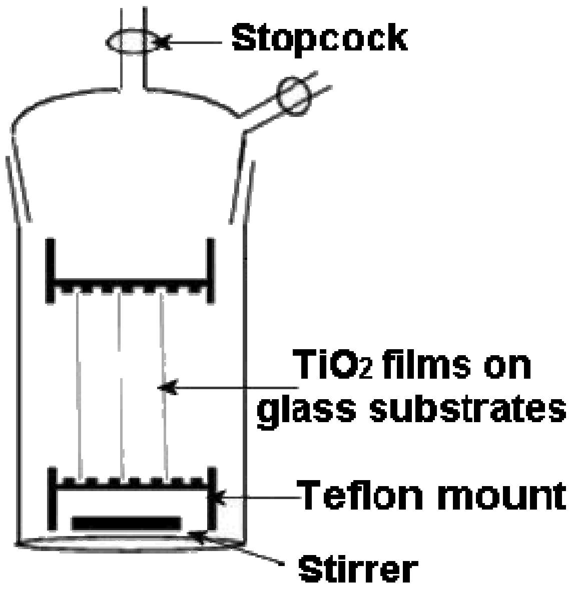
Kr adsorption ⇒ proves porosity



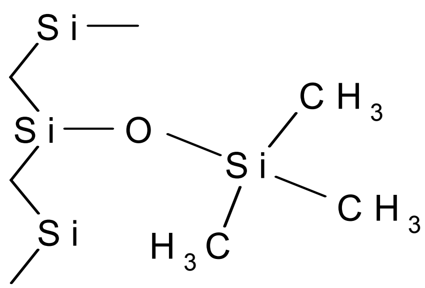
M. Wark, H. Wellmann, J. Rathousky, A. Zukal, Stud. Surf. Sci. Catal. 142 (2002), 1457



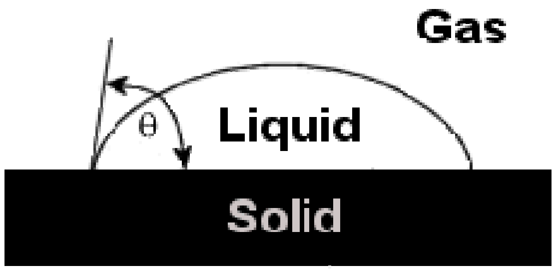
Mesoporous TiO_2 films: Hydrophobization



- Outgassed films functionalized with hexamethyldisilazane
  ⇒ methyl groups on surface of the pores



- Heated to 100°C, and revolved for 68 hours.

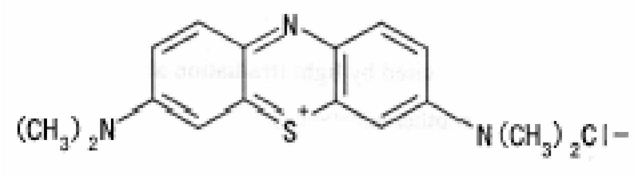


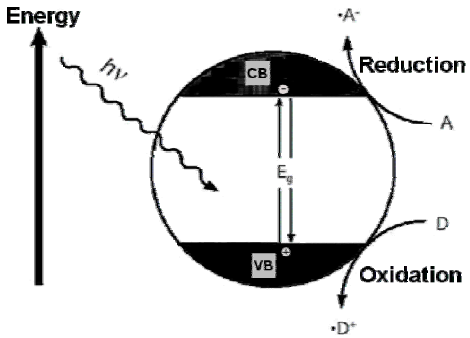
Contact angles with water:

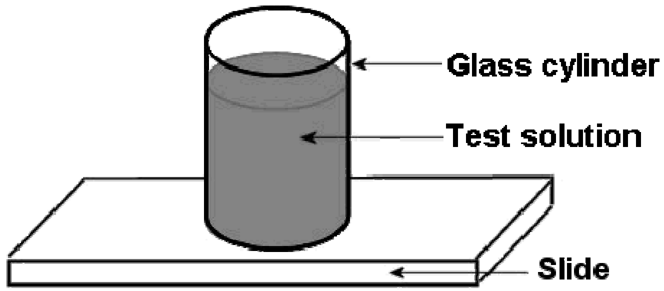
Film	Withdrawal rate (mm/s)	Contact angle (°)
TiO_2	1	< 5
TiO_2	2	< 5
TiO_2/hydrophob.	1	44.6
TiO_2/hydrophob.	2	48.5

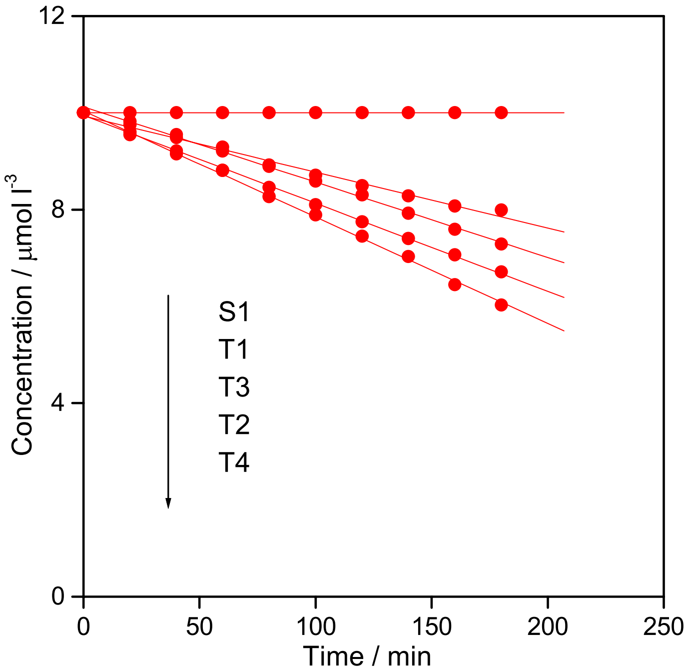
Hydrophobized mesoporous TiO_2 films: Photocatalysis

Degradation of methylene blue







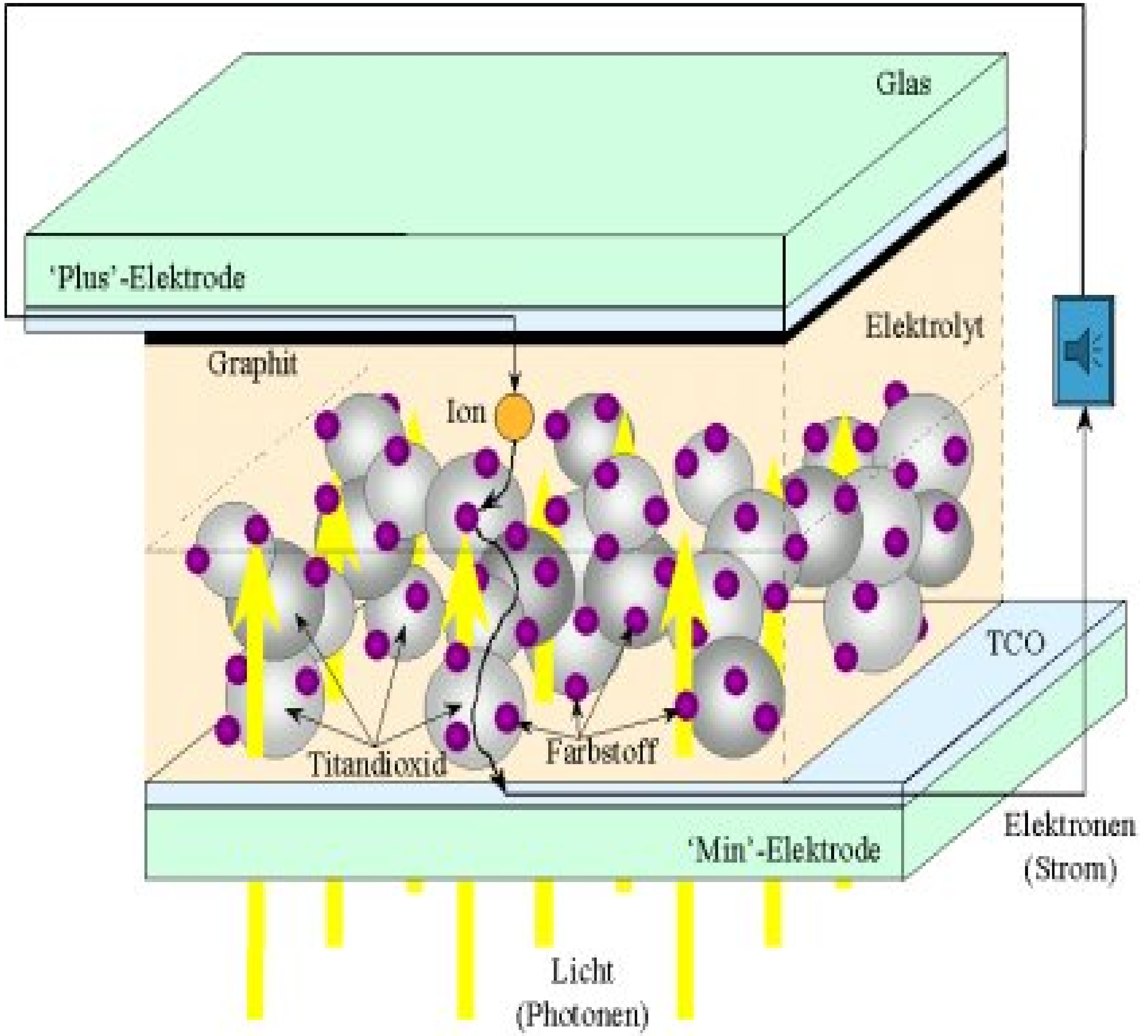


Film	Withdrawal rate	Photonic efficiency
T1: TiO_2	1 mm/s	0.0186
T2: TiO_2	2 mm/s	0.0291
T3: TiO_2/hydrophob.	1 mm/s	0.0250
T4: TiO_2/hydrophob.	2 mm/s	0.0352
S1: SiO_2	2 mm/s	0
Films of 4 nm TiO_2 particles		0.01 – 0.05

J. Tschirch, M.Wark et al.
Microp. Mesop. Mater., in press.

Hydrophobization improves adsorption of methylene blue

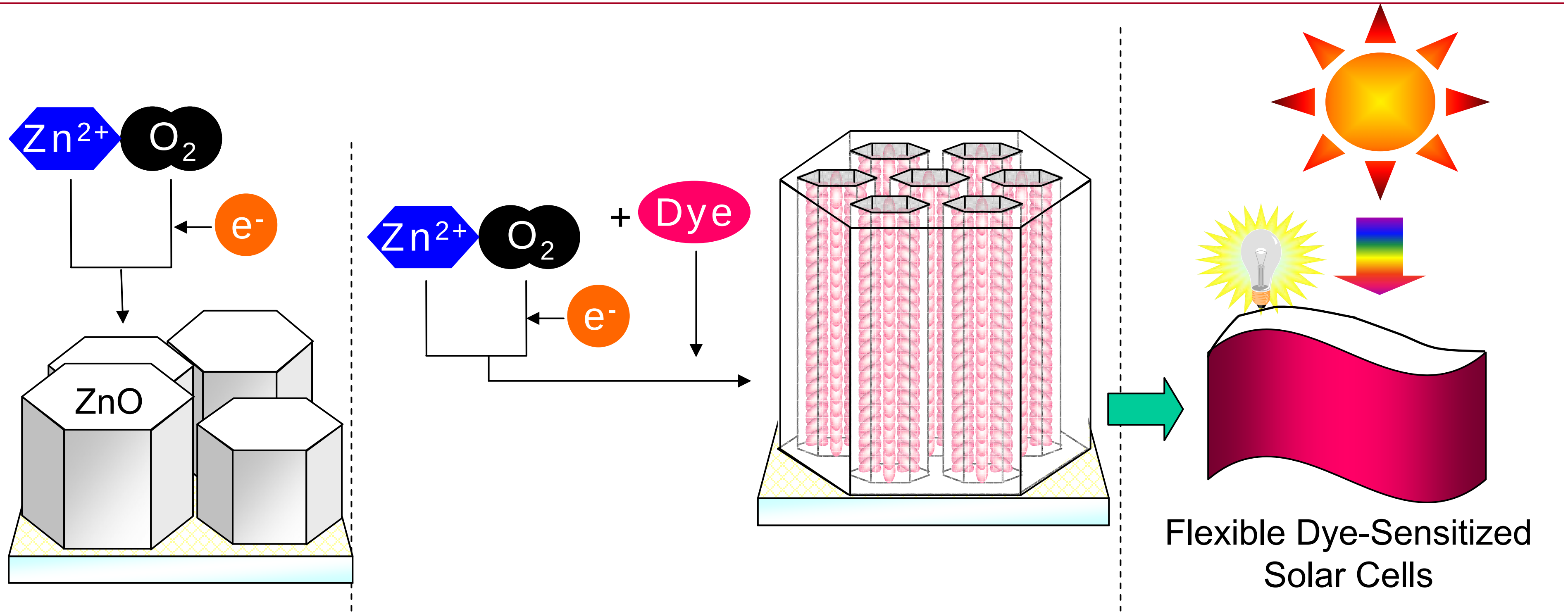
Design of dye-sensitized solar cells



http://www.mansolar.com/funktion.htm

- nanostructered TiO_2 film on conductive glass electrode
- monolayer of dye adsorbed on the TiO_2 surface
- J^-/J_3^- redox couple as electrolyte
- conductive glass coated with graphite or platinum as counter electrode

Electrodeposition of ZnO or TiO_2 / dye hybrid thin films

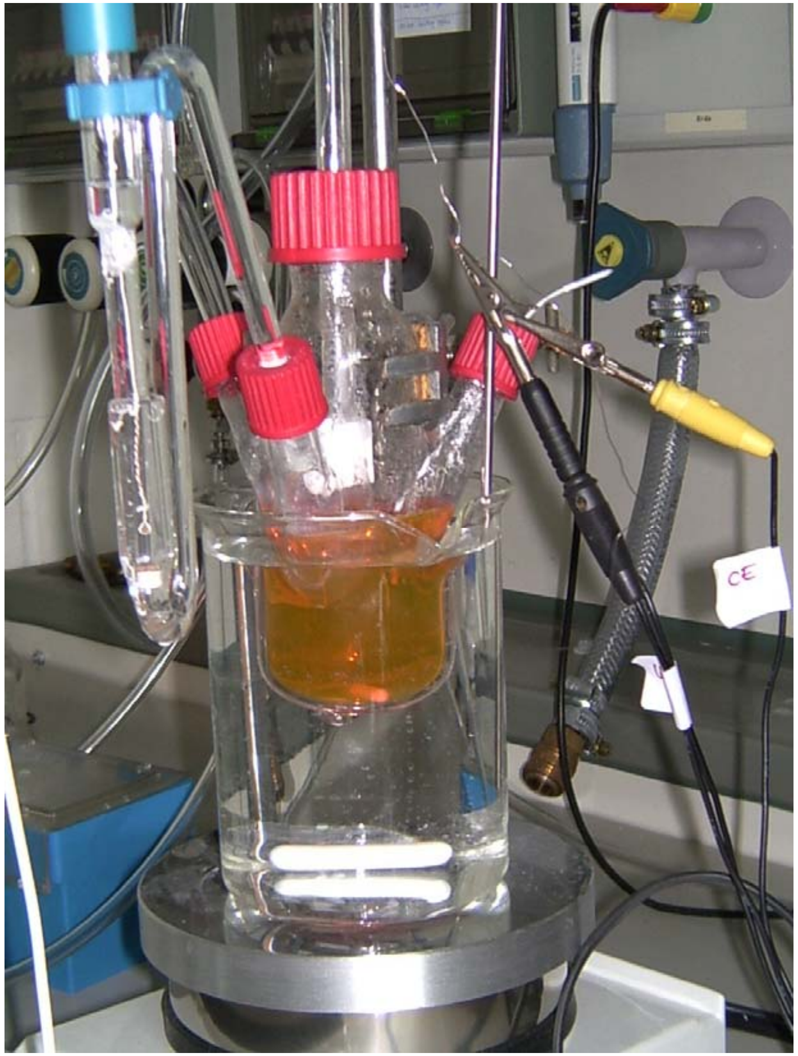


$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^-$
(E^0 = +0.246 V vs. SCE)

$Zn^{2+} + 1/2\ O_2 + 2e^- \rightarrow ZnO$
(E^0 = +0.69 V vs. SCE)

This route is followed by the group of Dr. T. Oekermann (Physical Chemistry, Univ. Hannover)

Experimental Setup



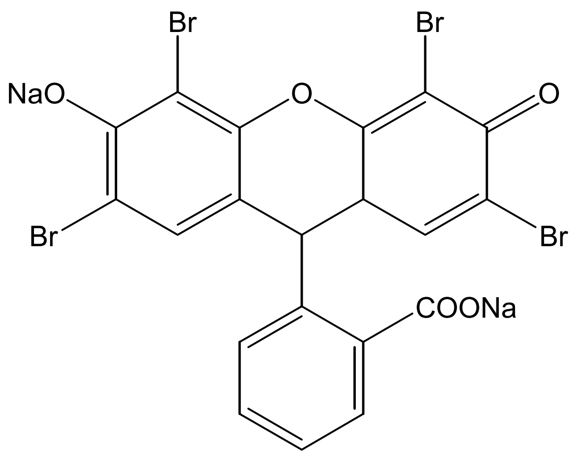
<u>3-electrode set-up</u>

reference electrode: Ag/AgCl

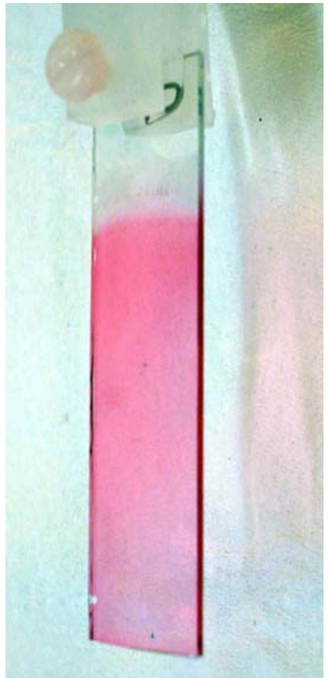
working electrode: FTO glass as substrate

counter electrode: zinc wire

With Eosin Y as dye:



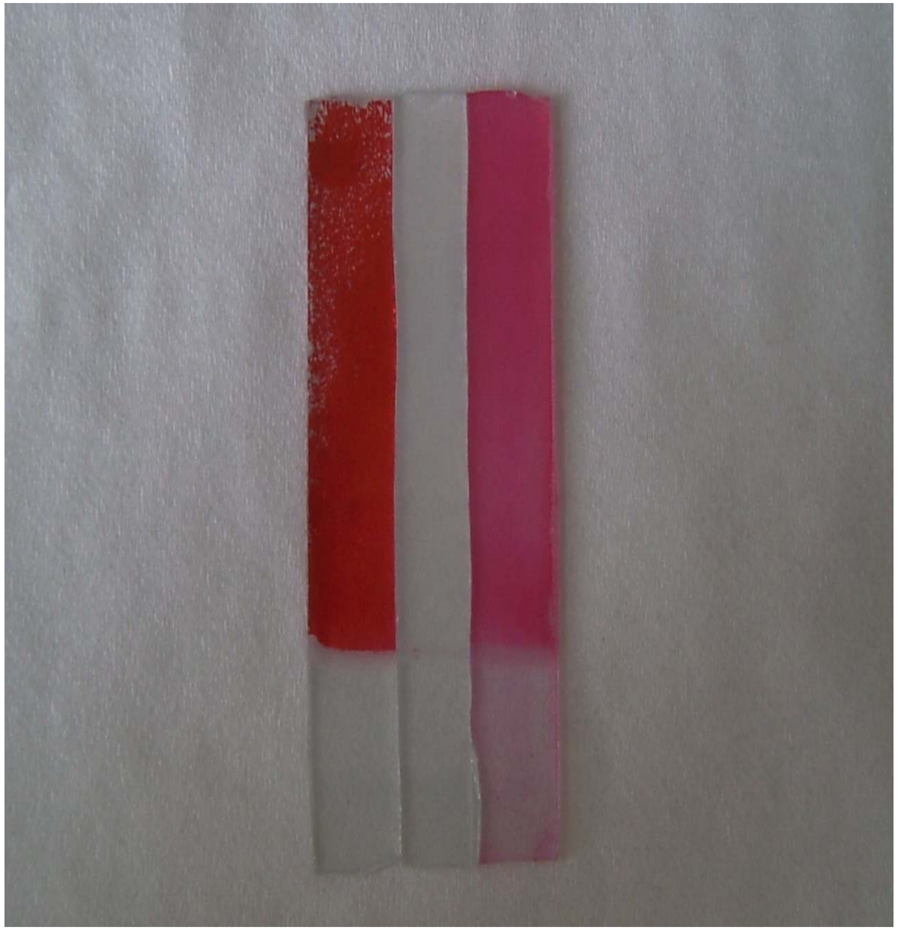
Eosin Y



Desorption and re-adsorption of dye

desorption:
6 h in KOH-solution (pH 10.5)

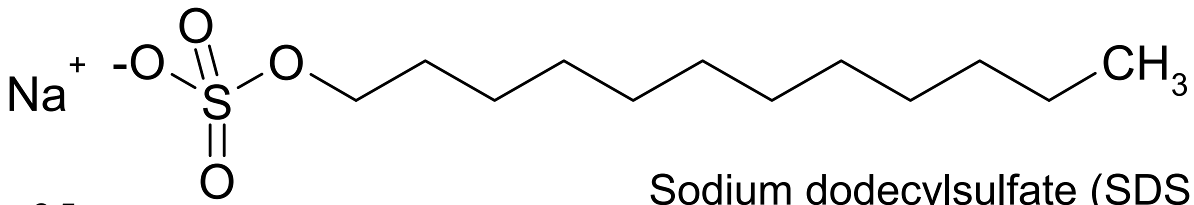
re-adsorption:
10 min in 0.5 mM ethanolic solution (boiling)



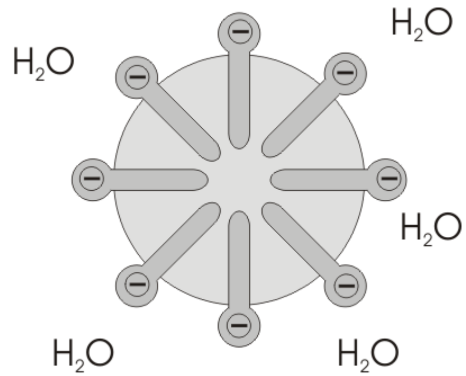
from left to right: ZnO/EY film as deposited, ZnO/EY desorbed, ZnO/EY re-adsorbed

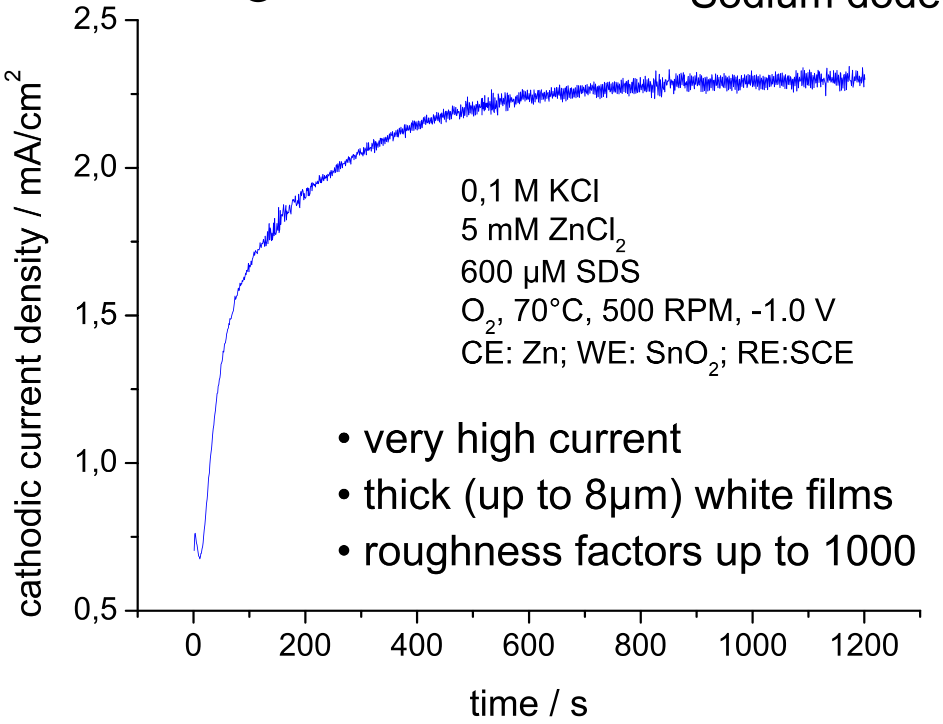
Highly porous electrochemically deposited ZnO or TiO_2 films

Electrodeposition in presence of a surfactant (micelle formation)

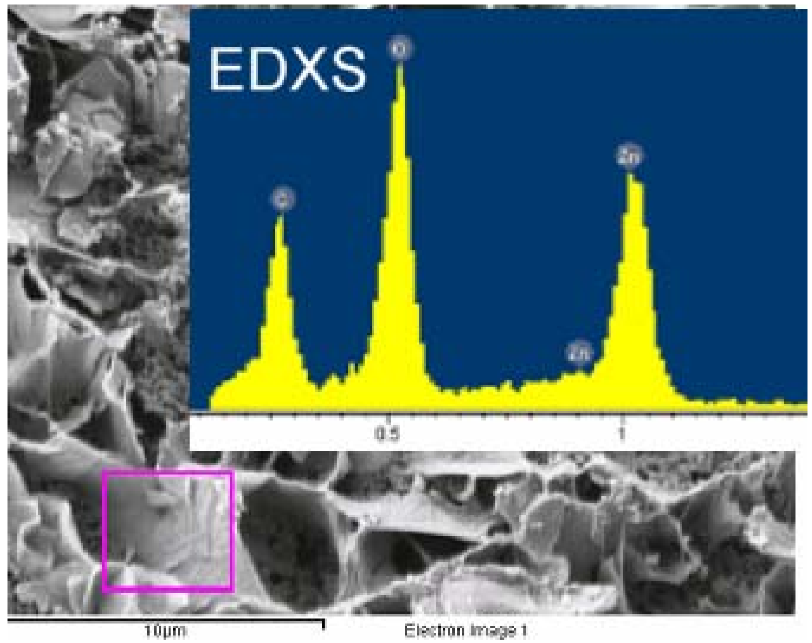


Sodium dodecylsulfate (SDS)



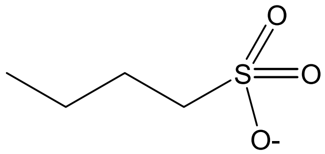


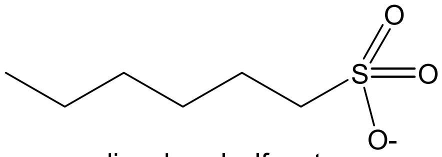
- very high current
- thick (up to 8µm) white films
- roughness factors up to 1000

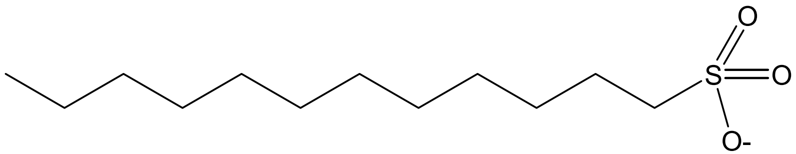


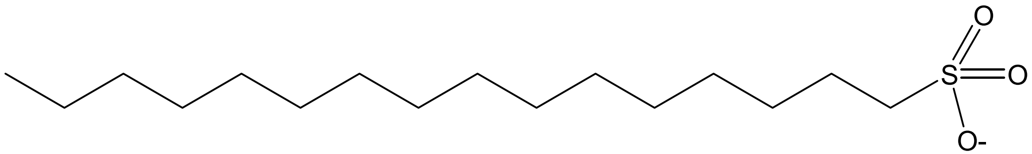
E. Michaelis, M. Wark et al., Thin solid films, **2005**, submitted

Different sulfonates as additives

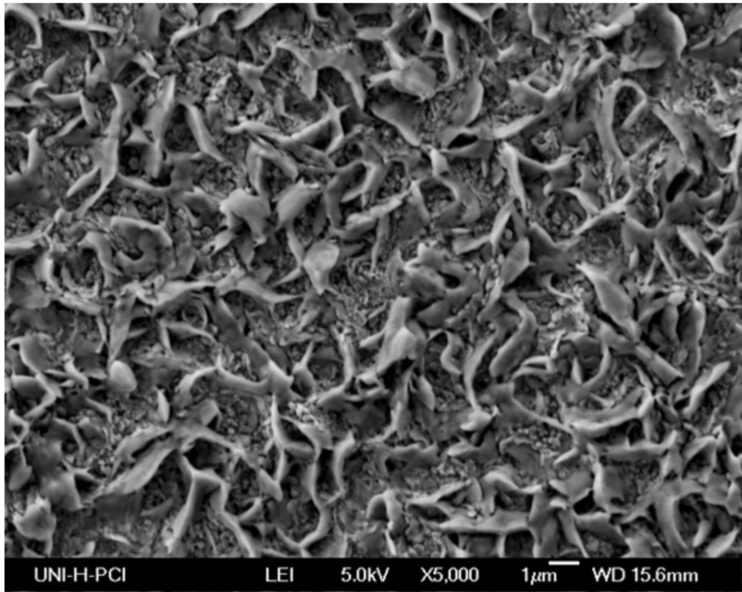

sodium butylsulfonate

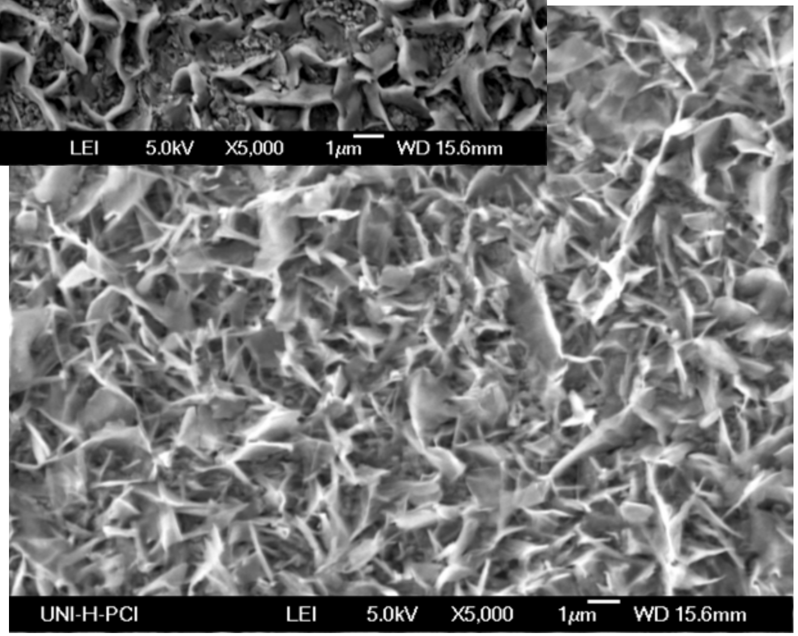

sodium hexylsulfonate


sodium dodecylsulfonate


sodium hexadecylsulfonate

Dodecylsulfonate
⇒ few lamellars



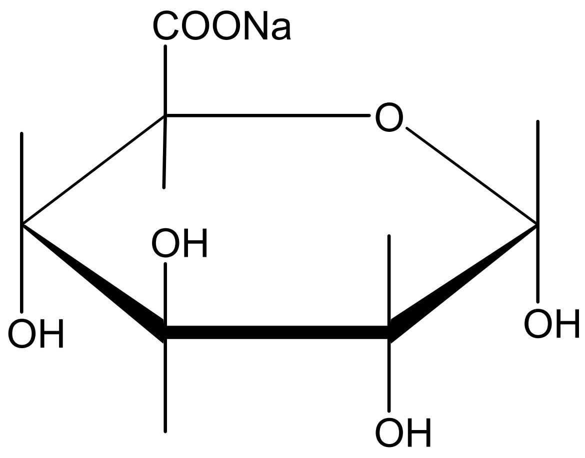


C. Boeckler, T. Oekermann,
unpublished results

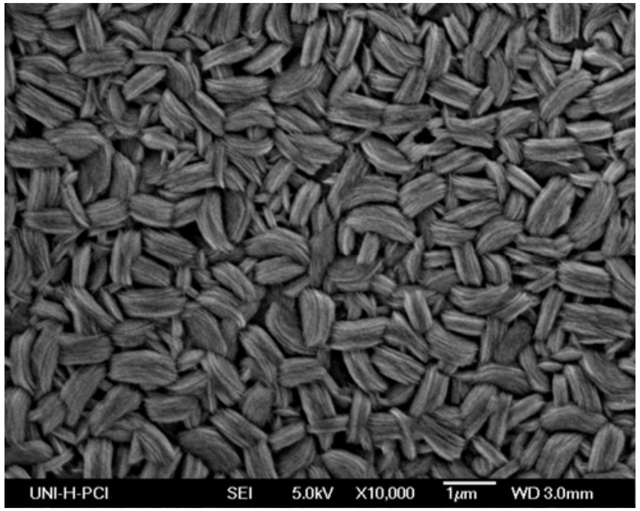
Hexadecylsulfonate, micelles can be formed ⇒ highly porous

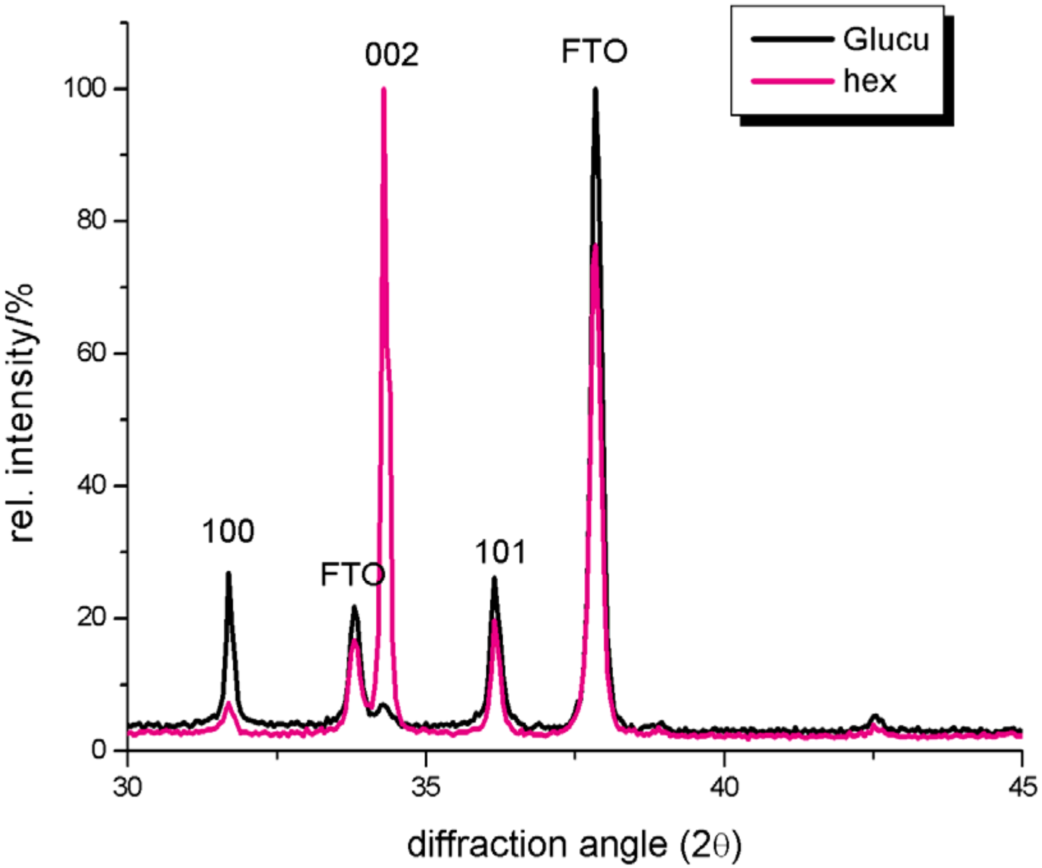
Sugar molecules as additives

C. Boeckler, T. Oekermann, unpublished results



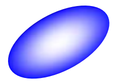
sodium glucuronic acid



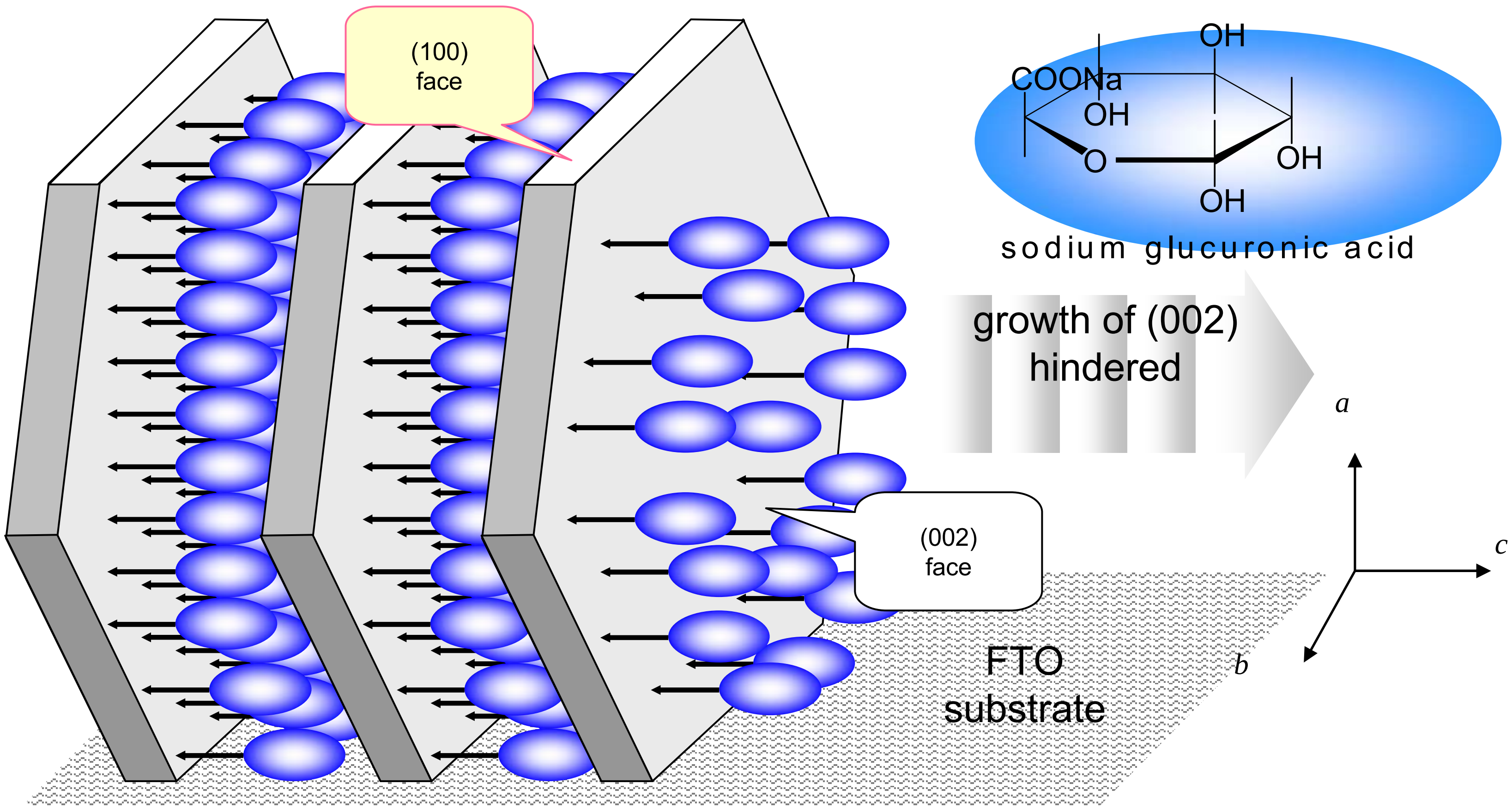


strong 110 orientation

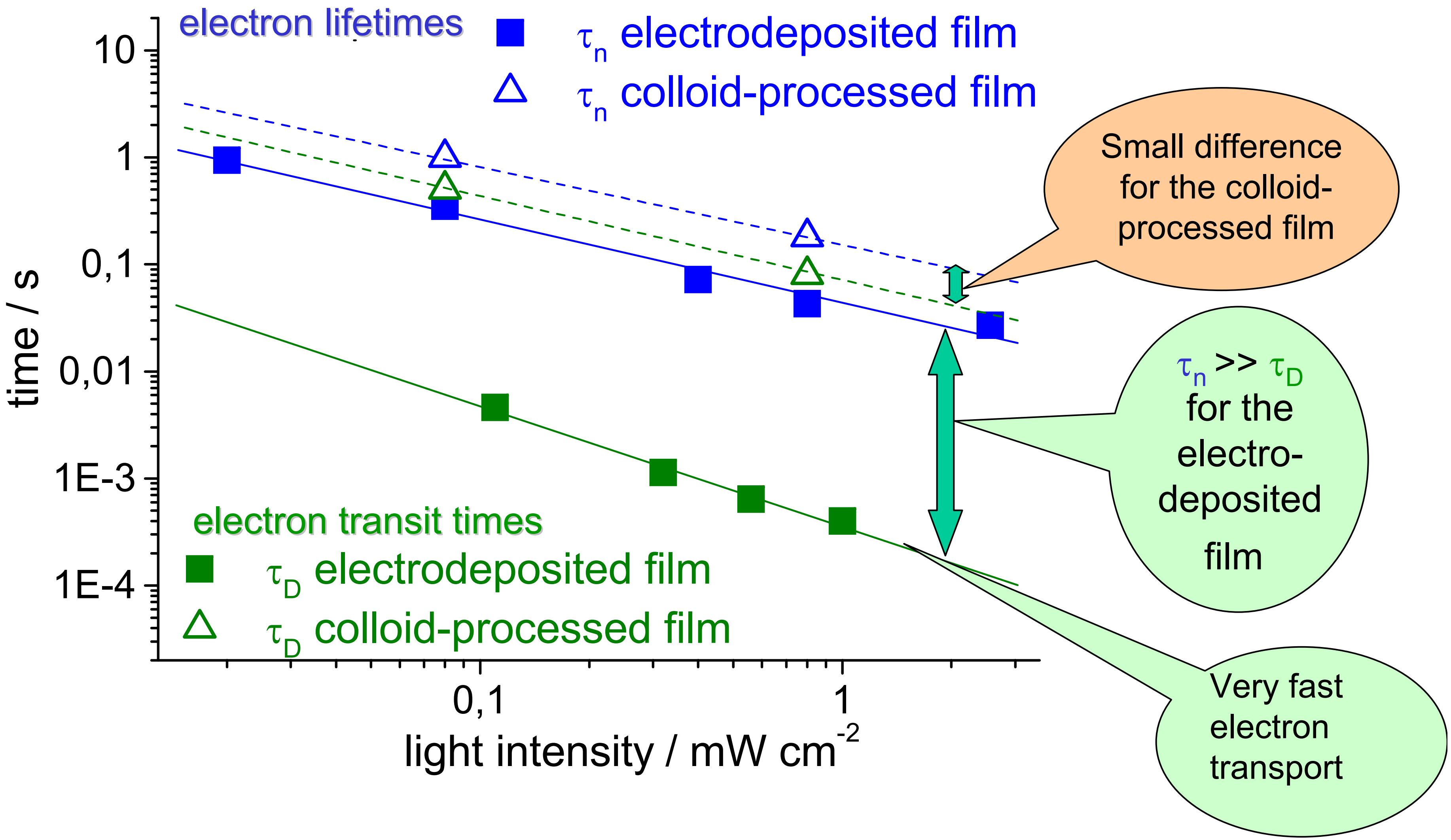
Growth model



C. Boeckler, T. Oekermann, unpublished results

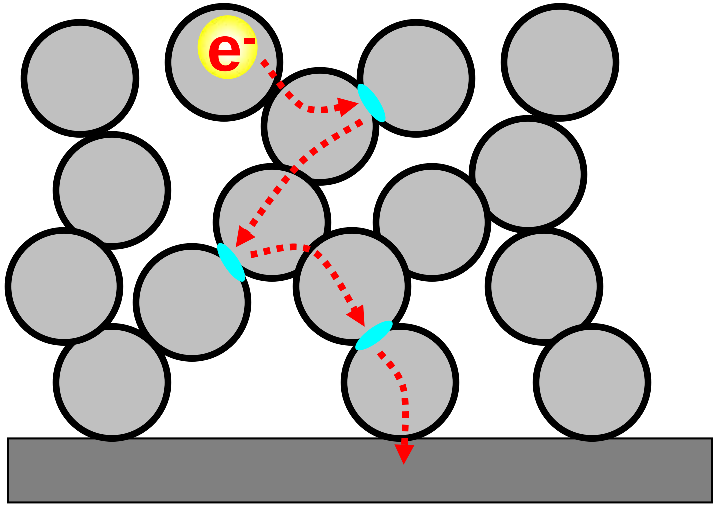


Electron transport in ZnO / Eosin Y films



Qualitative Model of Electron Transport in the ZnO films

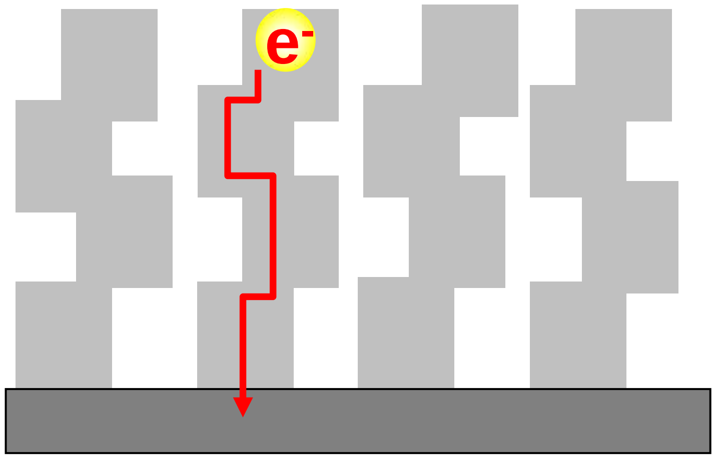
Colloid-processed ZnO
Nanocrystalline Film



- Grain boundaries
- Electron traps ( )

Slow electron transport

Electrodeposited ZnO
Nanoporous film



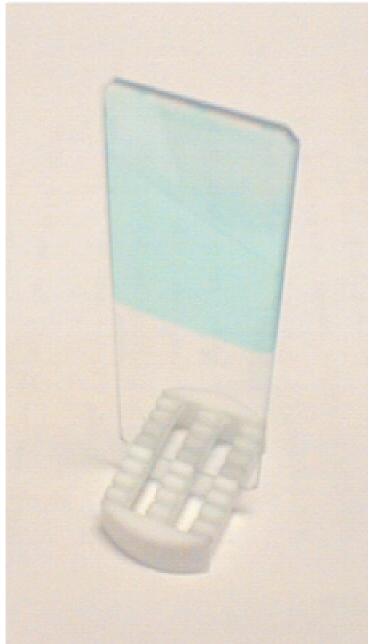
- Lower number of grain boundaries
- Rather ordered structure

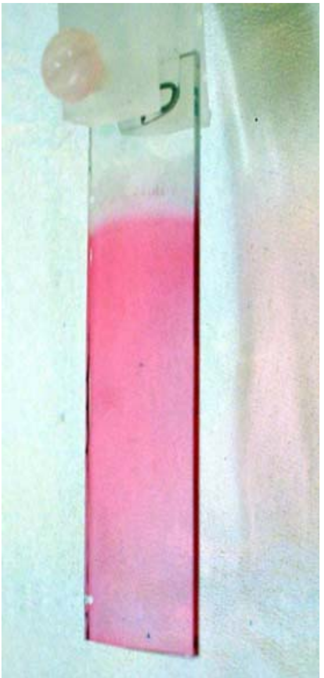
Fast electron transport

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

Conclusions

- On the inner walls of porous silica as well as titania films different functionalities (e.g. nanoparticles, dyes, hydrophobic groups) are anchored by covalent or ionic bonding. Use in e.g. optical data storage, photocatalysis, sensing, etc.





- Dye-sensitized oxide electrodes (ZnO or TiO_2) can be deposited electrochemically in a one-step method. These materials are promising for the development of new colored and flexible solar cells.

Thanks to:

- Dr. Hartwig Wellmann (CdS and CdSe in mesoporous SiO_2),
- Dr. Yven Rohlfing (optical switching),
- Dr. Dina Fattakhova (electroactive porous oxide films),
- Cand. Chem. Jessica Tschirch, Prof. Dr. D. Bahnemann (photocatalysis),
- Dr. Torsten Oekermann, Cathrin Boeckler, Katrin Wessels,
  Dr. Esther Michaelis (ZnO electrodes),

- Dr. Armin Feldhoff (Hanover) , Dr. Frank Krumeich (Zurich) - TEM
- Dr. Jiri Rathousky (Prague) - Kr adsorption

- Prof. Dr. Jürgen Caro – head of the group

- DFG, VW foundation, Volkswagen AG - funding

Thank you for your kind attention !!!