Institut für Physikalische Chemie und Elektrochemie

Chemische Nanomaterialien

Womit trägt die Physikalische Chemie der Uni Hannover zum Gelingen des LNQE bei?

Die vorgestellten Arbeiten wurden mehrheitlich unter dem Dach des Zentrums für Festkörperchemie und Neue Materialien erarbeitet.

Arbeitsgruppen des PCI

Prof. Caro
Nanostrukturierte Wirt/Gast-Systeme und Funktionsschichten
- PD Dr. Wark
- Dr. Oekermann
- Dr. Feldhoff

Prof. Becker
Kleinste Festkörperteilchen und Mikrowellenspektroskopie
- Dr. Grabow

Prof. Heitjans
Dynamische und kinetische Prozesse an Festkörpern

Prof. Imbihl
Dynamische Prozesse an Oberflächen

PD Dr. Michael Wark

Deposition of porous sol-gel layers

Functionalization of porous materials

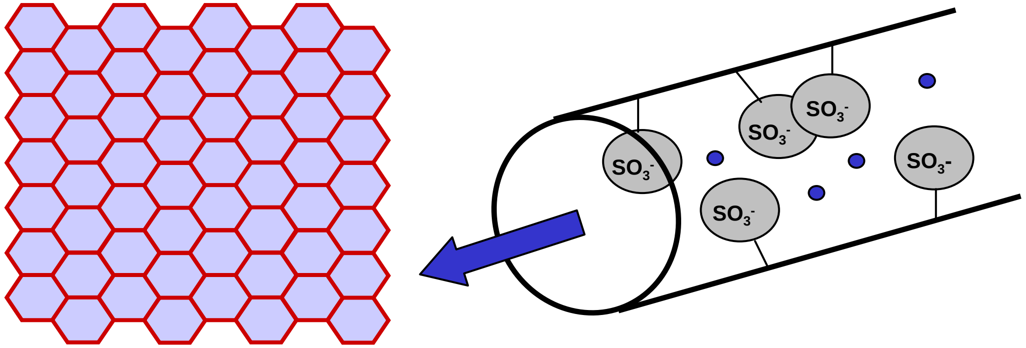
Proton conducting membranes for fuel cells

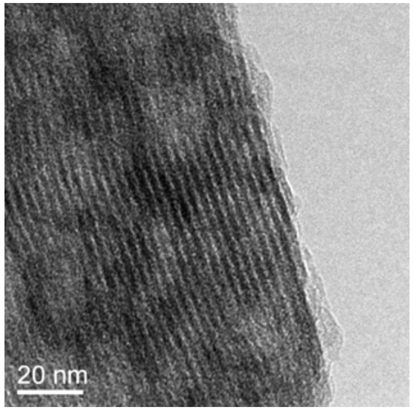
Inorganic nano-tubes

UV-vis spectroscopy of solids

Mesoporous SO_3H-functionalized SiO_2 with > 1000 m^2/g

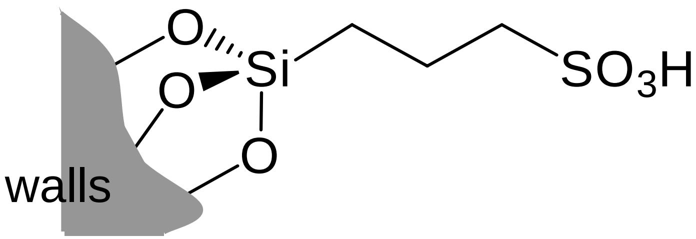
Functionalized mesoporous oxides (SiO_2) for proton conductivity <u>and</u> water storage
(⇒ additives for PEM fuel cell membranes)



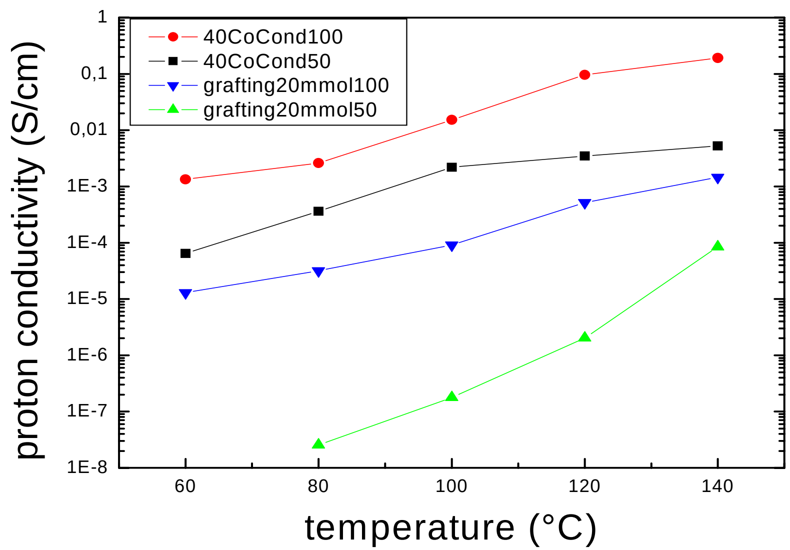


<u>Two methods for loading</u>:

1. postsynthetic grafting with thiol-silane and oxidation.
2. Co-condensation: addition of thiol-silane direct to synthesis gel for mesop. SiO_2, oxidation simultaneously to template removal.



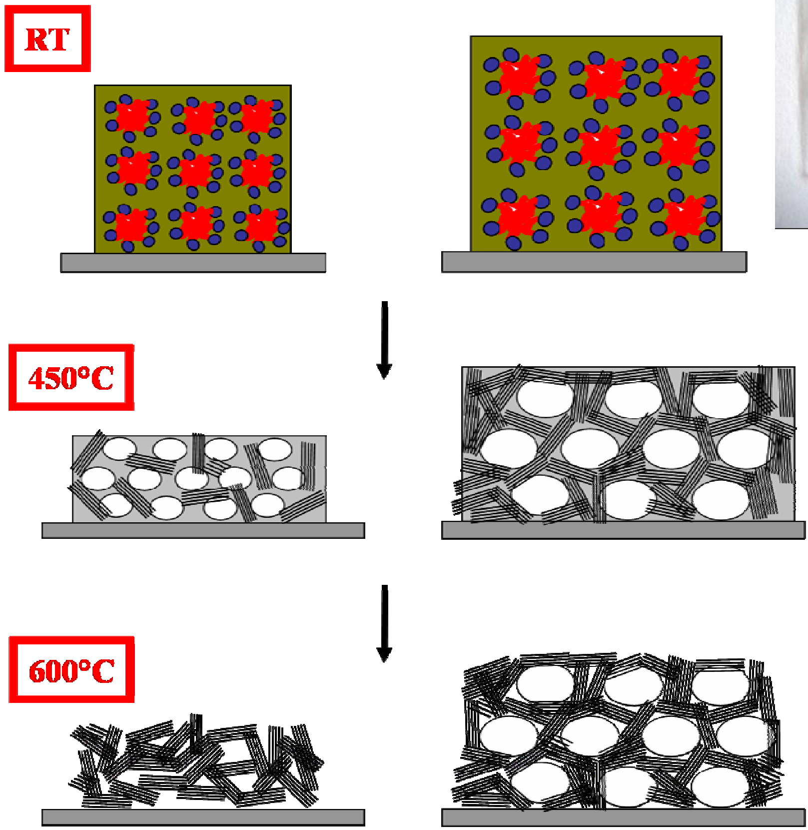
Loading and, thus proton conductivity higher for samples formed by co-condensation

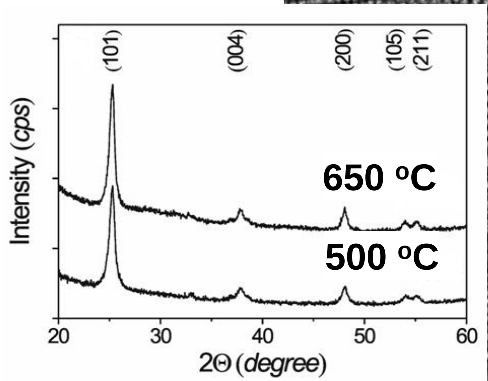


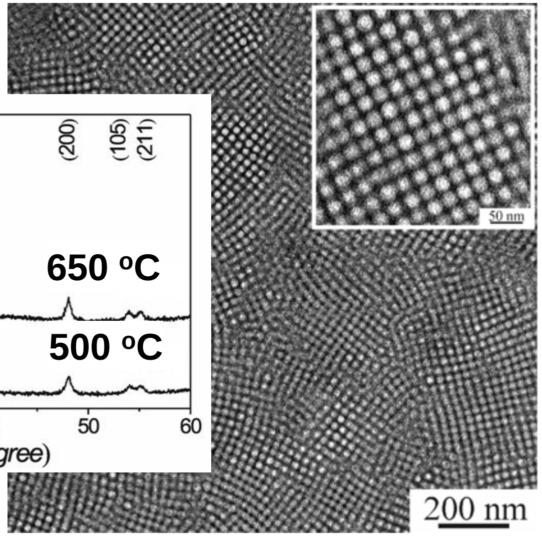
Mesoporous TiO_2 films with highly crystalline walls

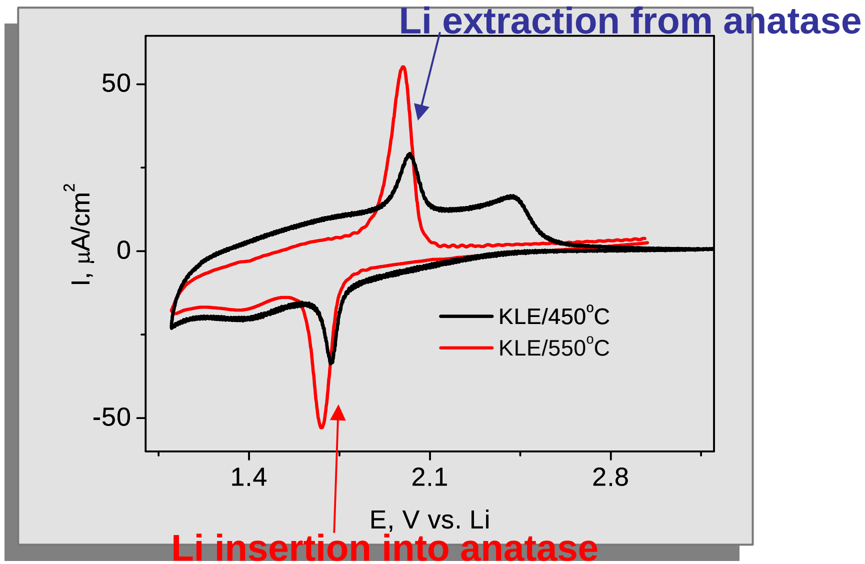
Mesoporous TiO_2 films, made by template-assisited sol-gel chemistry, dip-coating (EISA process)

earlier films (template: Pluronic) | new films (template: KLE)









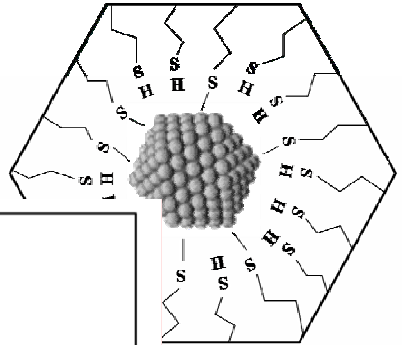
KLE block copolymer

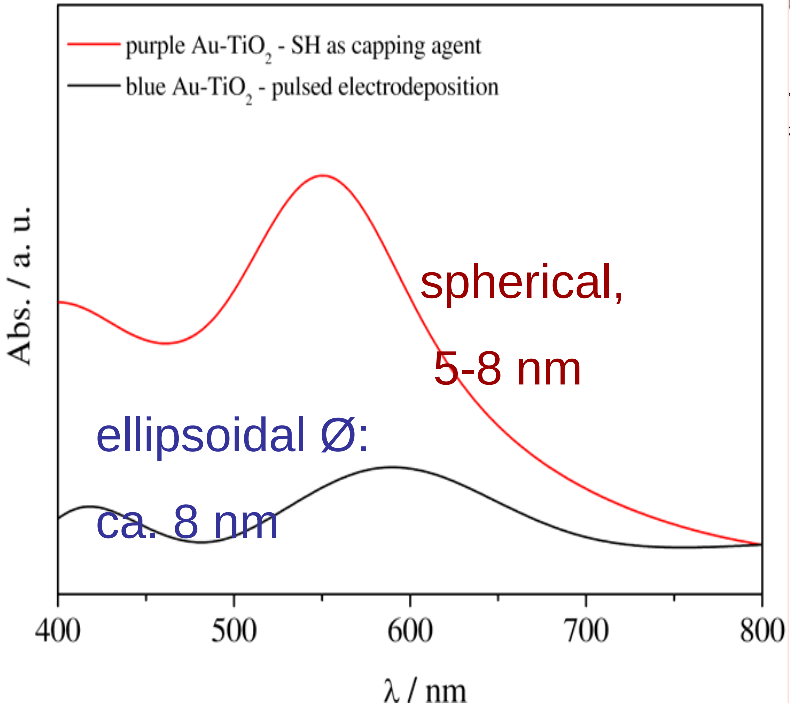
$H(CH_2CH_2CH_2(CH)CH_2CH_3)_{89}(OCH_2CH_2)_{79}OH$

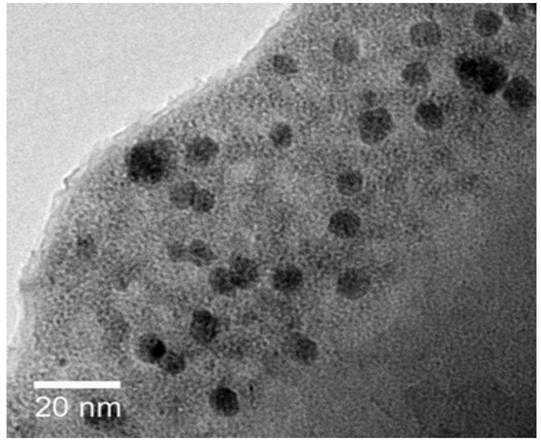
D. Fattakhova-Rohlfing, M. Wark et al., Adv. Funct. Mater., 17 (2007), 123.

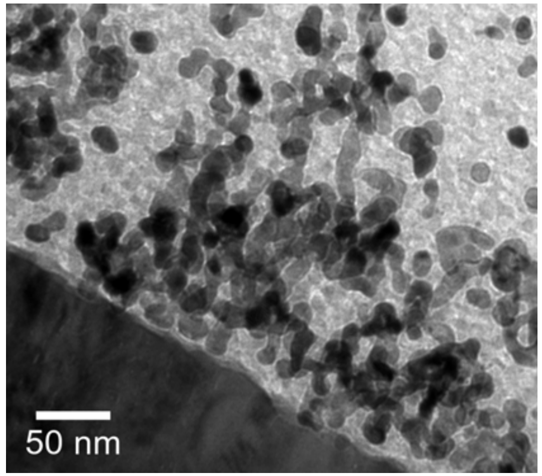
Au nanostructures in mesop. TiO_2 films – plasmon resonance

- Anchoring of Au^{3+} ions on thiol groups
- Reduction with $NaBH_4$









- Pulsed electrochemical deposition; starting with very short, negative potential pulse
- ⇒ generation of worm-like Au structures possible.

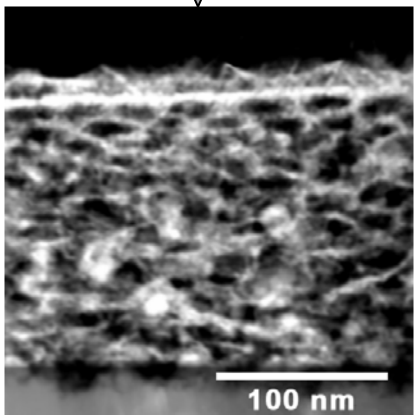
I. Bannat, T. Oekermann, M. Wark, et al., work in progress

Mesoporous conductive indium-tin-oxide (ITO)

Sol-gel precursor

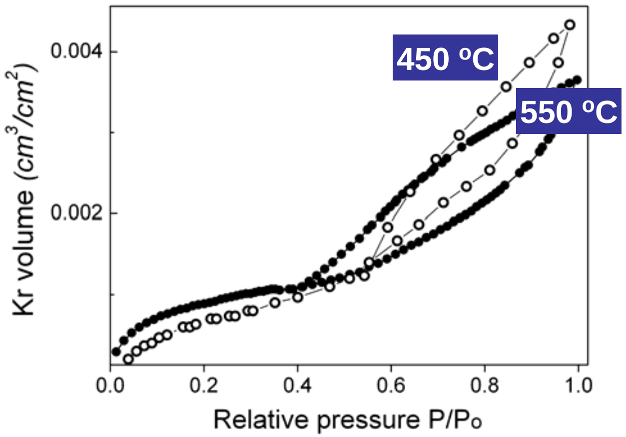
- In source: In(III) acetylacetonate (0.6 g)
- Sn source: Sn(IV) chloride (0.038 g)
- Template: KLE (0.085 g)

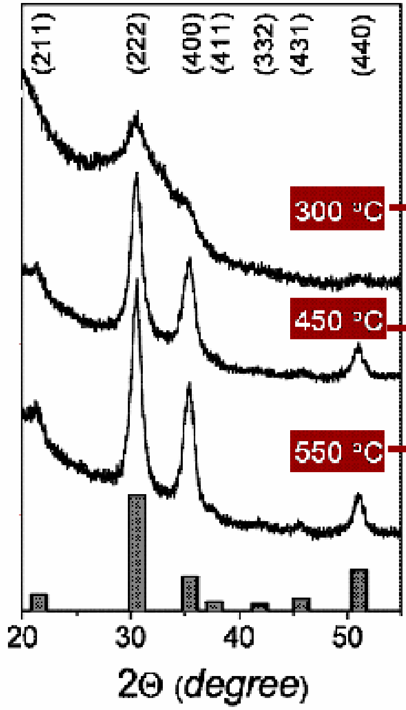
EISA process - Dip-coating - relative humidity 18-20 %



high porosity, but also high crystallinity of walls
⇒good electrical conductivity

Kr adsorption at 77 K





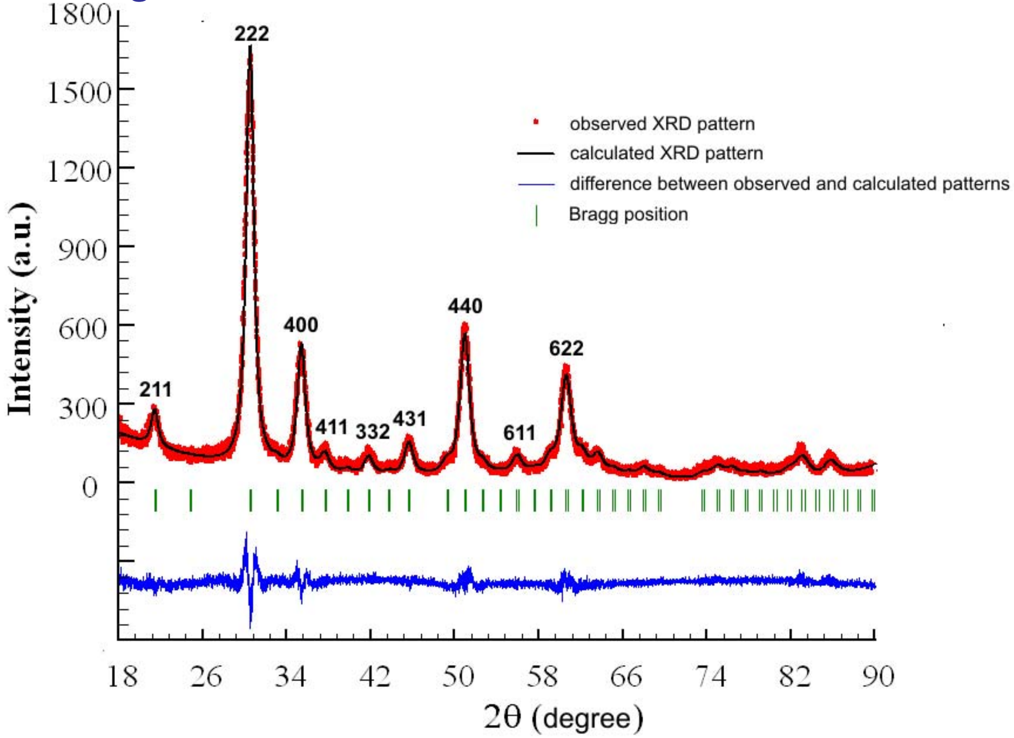
	Sheet resistance Ω	Specific resistivity Ω cm
300 °C	**Non-conductive**	
450 °C	**3 ·10^5**	**5**
550 °C	**1 · 10^4 (N_2)** **1.3 · 10^3 (H_2)**	**0.15** **0.02**

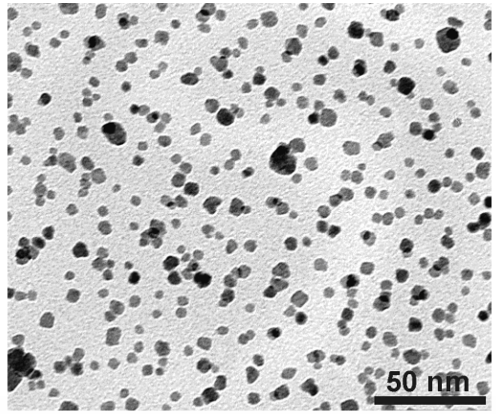
application:
new type of solar cells, electrochromism, electroluminescence, ….

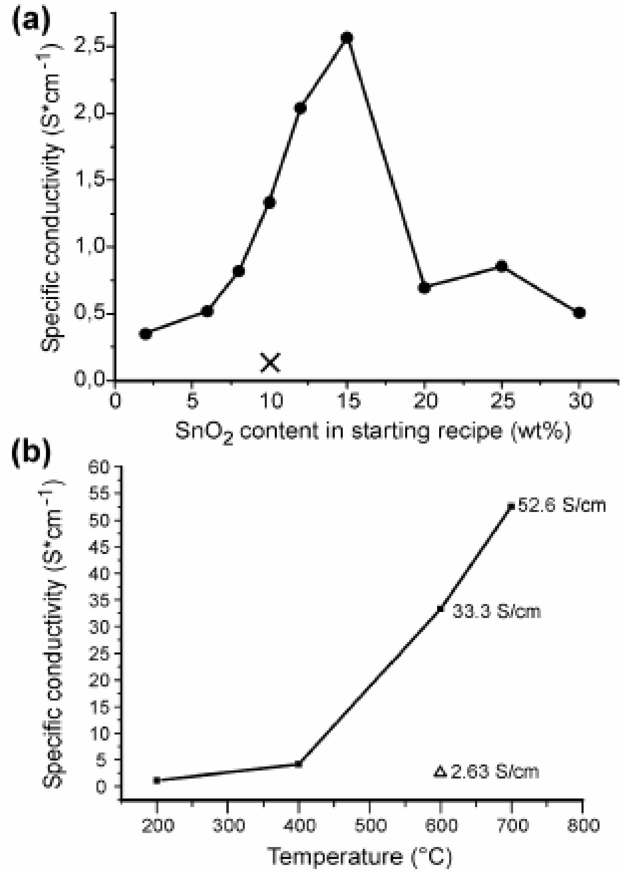
D. Fattakhova, T. Oekermann, M. Wark, et al., Adv. Mater.18 (2006) 2980

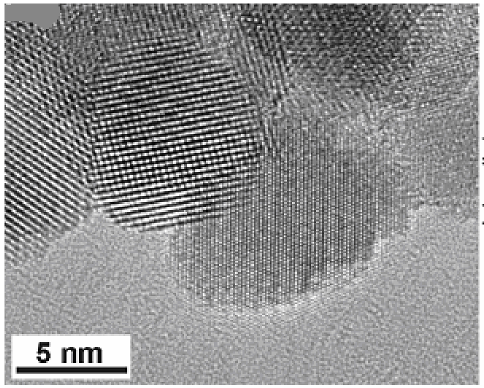
Well-crystalline ITO nanoparticles

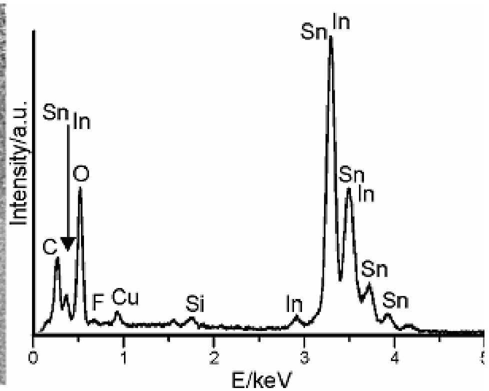
Non-aqueous synthesis of ITO nanoparticles from $In(acac)_3$ and $Sn(OtBu)_4$, heating in autoclave to 200°C for 48 h.





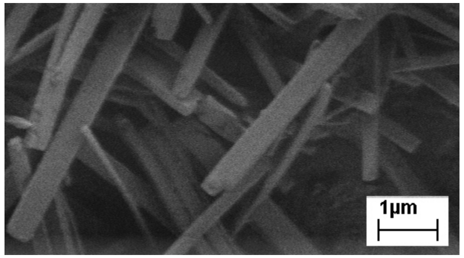


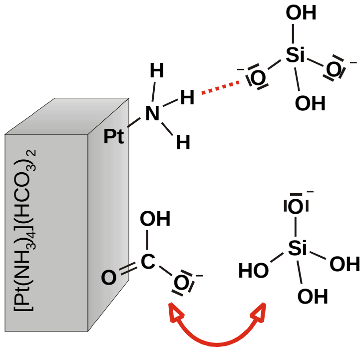


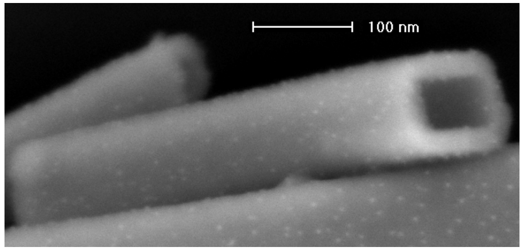


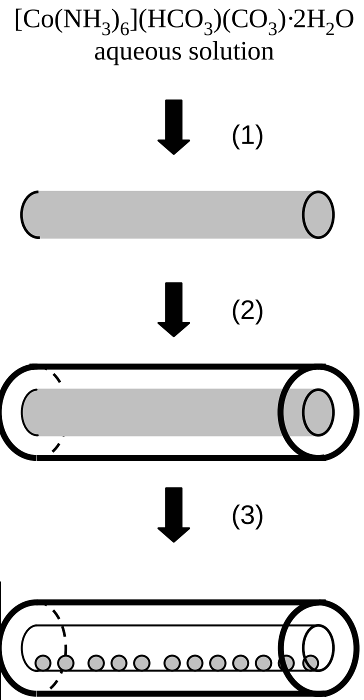
I. Ba, M. Niederberger, M. Wark, A. Feldhoff, et al. Chem. Mater. 18 (2006), 2848.

Controlled growth of metal containing oxide nanotubes (NTs)



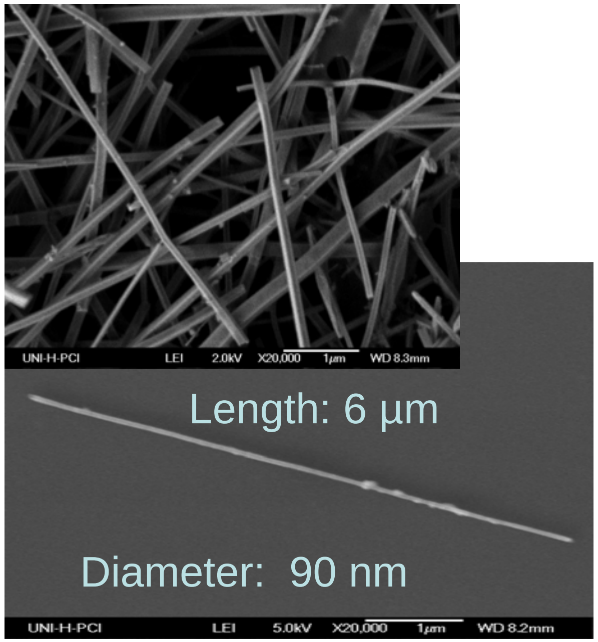




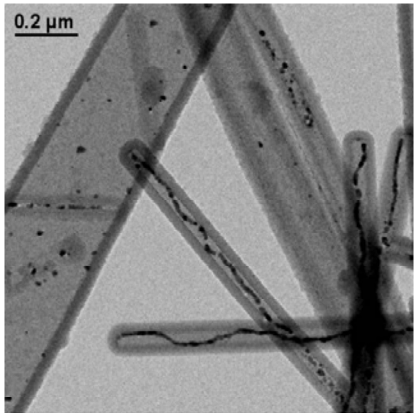


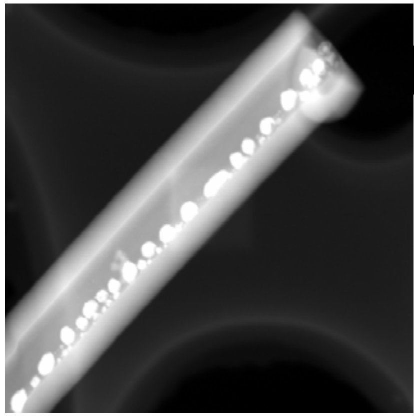
In a sol-gel process precipitated metal salt nanofibres work as templates to form NTs

Uniform SiO_2 or TiO_2 NTs with high aspect ratios



By reduction of the template salt, metal nanowires (but contacting of NTs difficult) or chains of nanoparticles (Co: interesting magnetic properties) form in the NTs.





L. Ren, M. Wark, Chem. Mater. 17 (2005), 5928.

Dr. Torsten Oekermann

- (Photo-)Electrochemistry

- Impedance spectroscopy

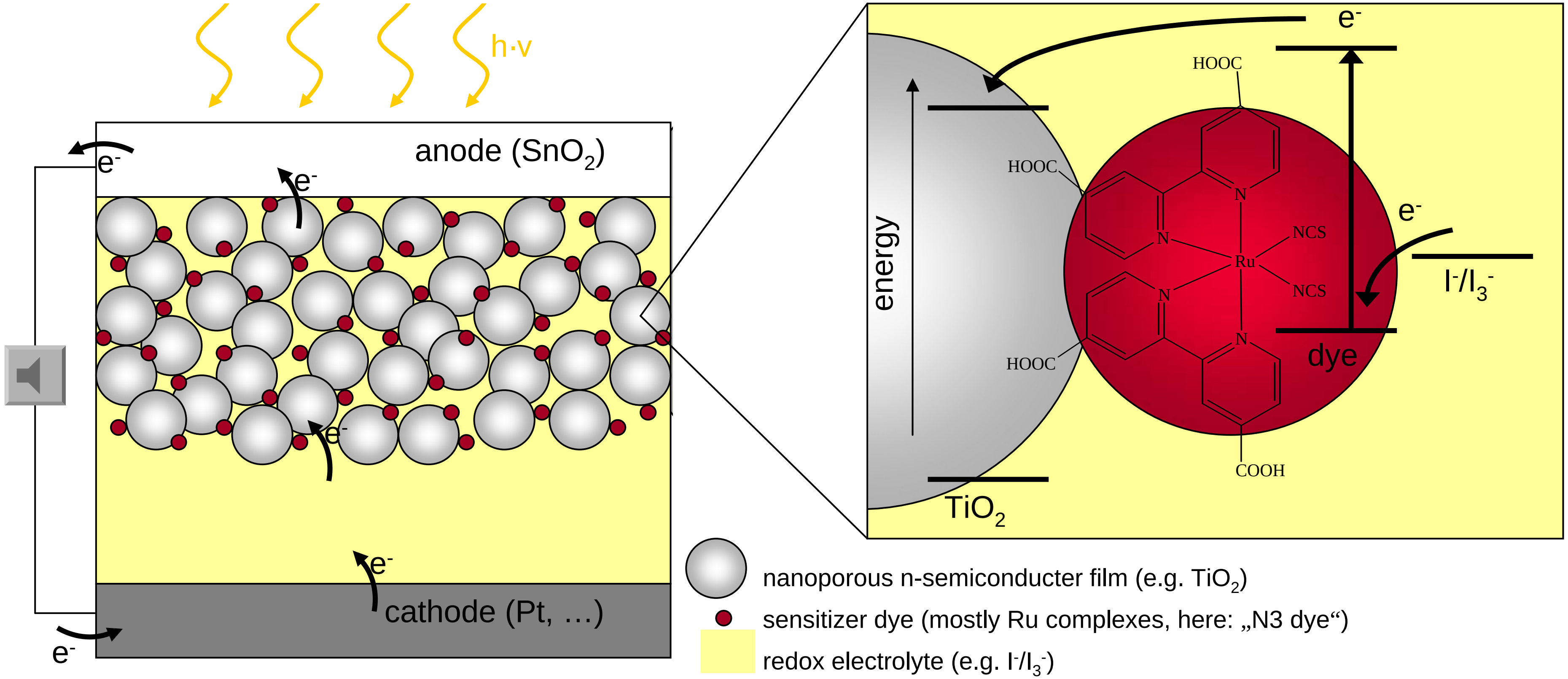
- Time- and frequency-resolved photoelectrochemical methods

- Electrochemical deposition of porous layers

- Dye sensitized solar cells

Alternative for silicon solar cells:

Dye sensitized solar cell (DSSC)



Preparation of porous semiconductor films for DSSC by

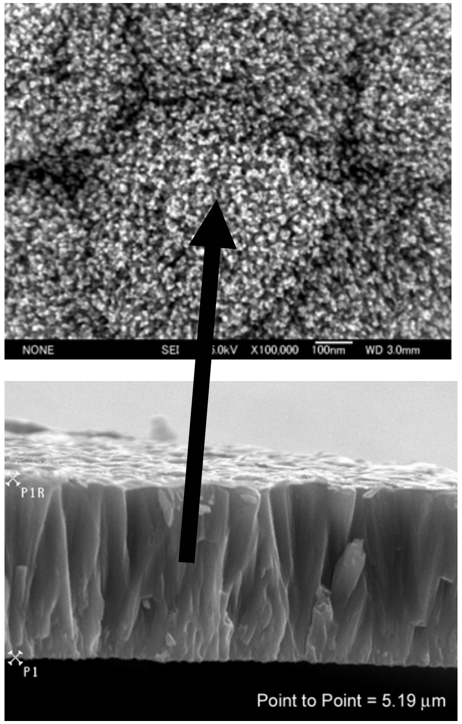
- colloid-processing from nanoarticles
- electrophoretic deposition of nanoparticles
- sol-gel methods (collaboration with M. Wark)

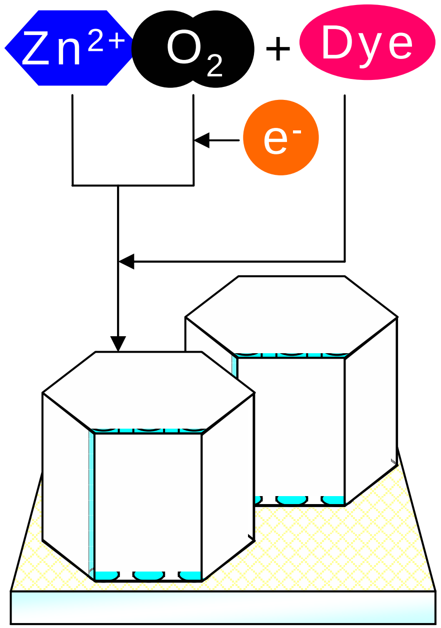
Oekermann, Wessels

Novel method: Electrochemical preparation of porous semiconductor films for DSSC

- Crystalline ZnO layer is formed by cathodic electrodeposition at T > 65 °C
- Dye molecules in the electrodeposition bath adsorb to the growing film and are incorporated

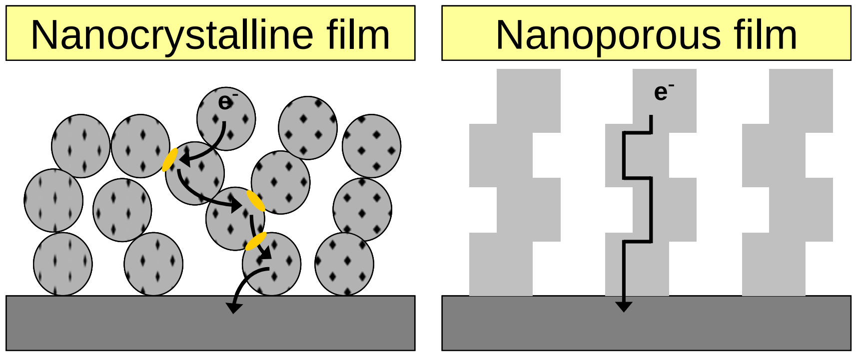
$$Zn^{2+} + \tfrac{1}{2}\, O_2 + 2e^- + \text{additive} \rightarrow ZnO\ \text{(porous)}$$





Colloid-processd film made from nanoparticles
→ slow electron transport

Electrodeposited film „porous single crystal“
→ fast electron transport



Oekermann, Boeckler et al., J. Phys. Chem. 109 (2005) 12560

Benchmarking: Comparison of the efficiency of three types of solar cells under realistic conditions

efficiency

Si single-crystal solar cell:
25 %

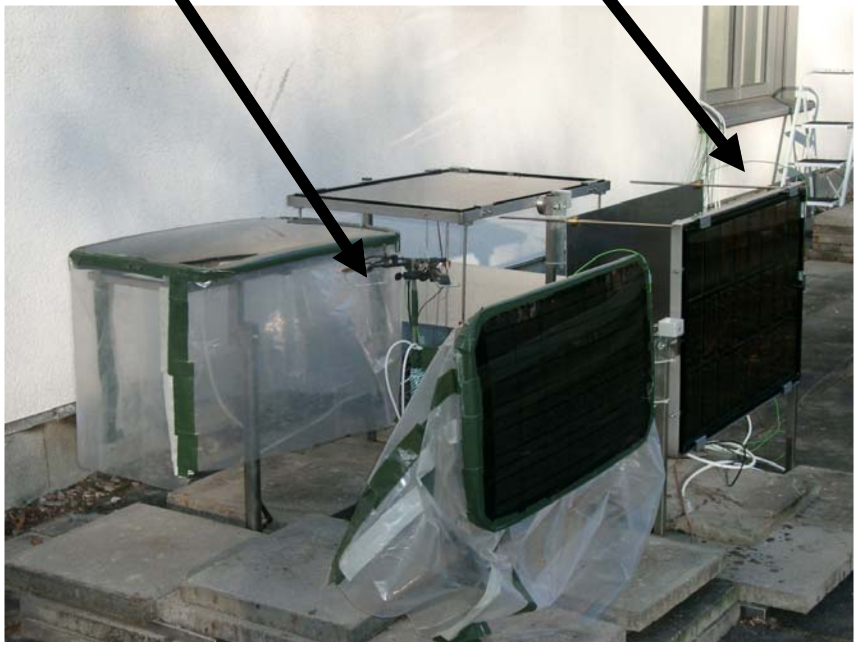
Dye-sensitized solar cell (à la Grätzel)
11,5 %

Dye-sensitized solar cell with electrodeposition of ZnO (à la Oekermann, Hannover, and Yoshida, Gifu, Japan)
6 % ⇒ World record for low-T prepared DSSC

costs

Sliding roof of the AUDI car = Si single crystal solar cell

Commercial DSSC of the company Great Cell



Testing facility on the institut's roof:

Cells in vertical and horizontal orientation

Oekermann, Marschall

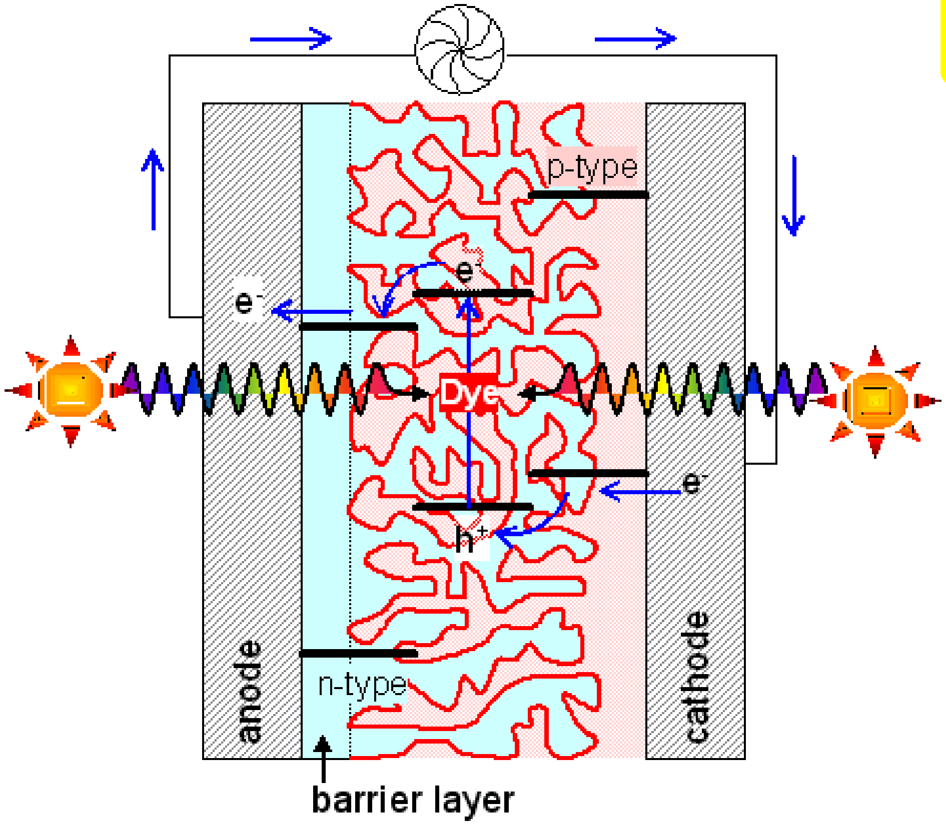
Aus Liebe zum Automobil

Novel concept: Dye-sensitized p-n- solar cells

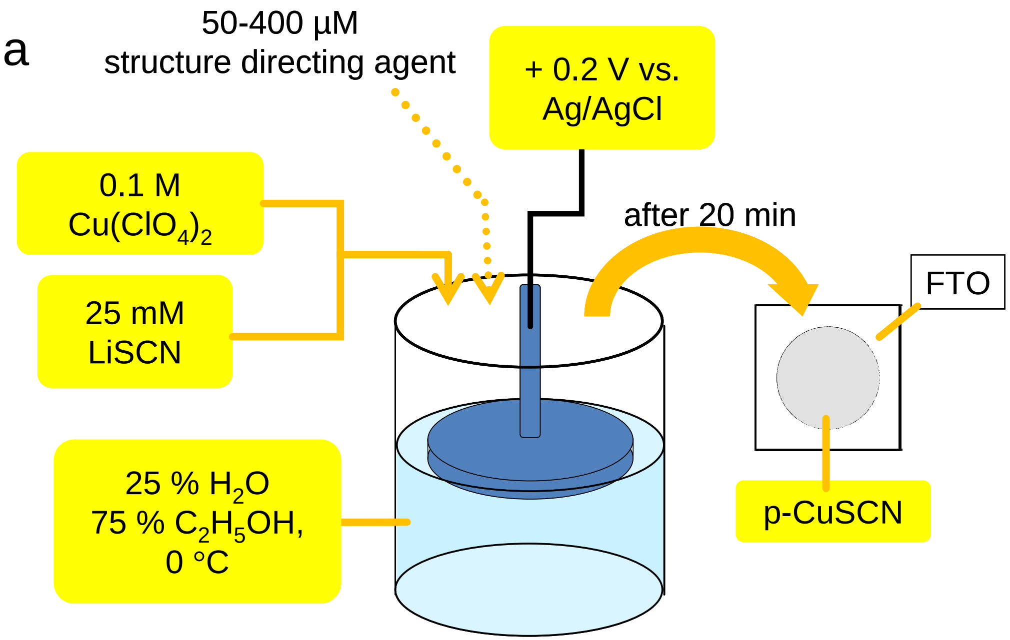
Replacement of the liquid electrolyte by a solid p-type semiconductor

→ Improved long-term stability

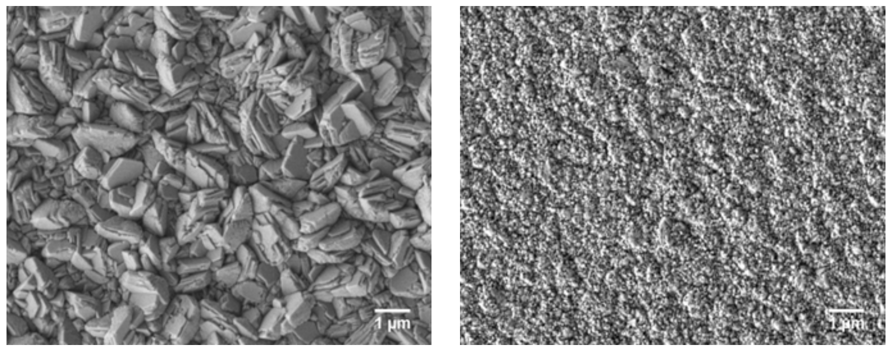
A promising material is p-CuSCN



Oekermann, Selk



$Cu^{2+} + SCN^{-} + e^{-} \rightarrow CuSCN$ **(nanocrystalline)**



SEM images of CuSCN films deposited with and without cetyltrimethylammonium bromide

Dr. Armin Feldhoff

Elektron microscopy: SEM, TEM

Micro structure analysis

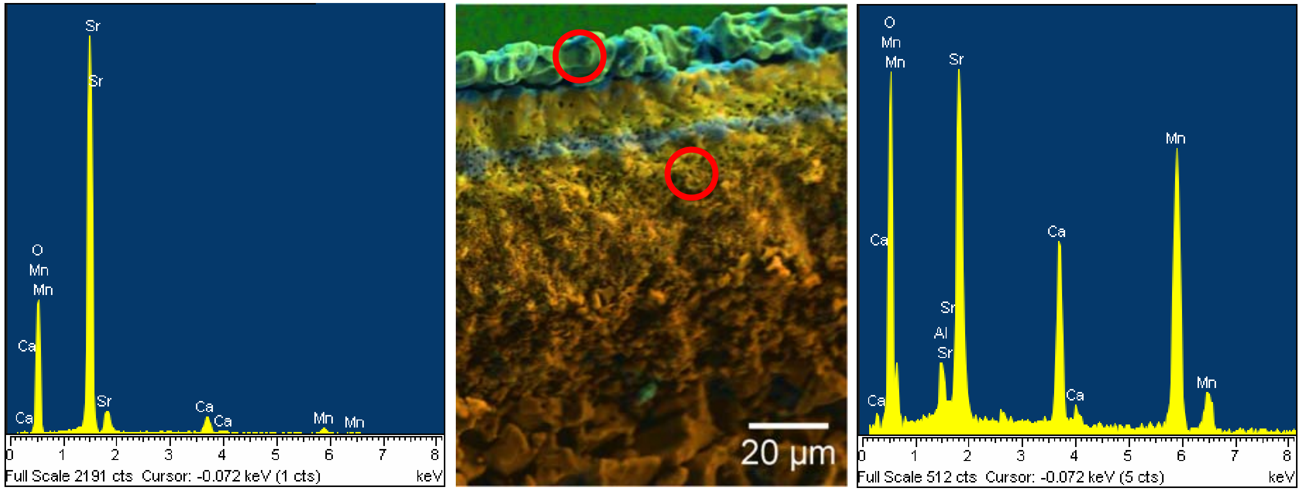
In situ XRD (under gas atmosphere up to 1200 °C)

- Sekundärelektronendetektor
- Semi-in-lens-Detektor für kleine Arbeitsabstände
- Rückstreuelektronendetektor (BSE)
- Energiedispersives Röntgenspektrometer (EDXS), Oxford Instruments INCA 300, Detektion ab Be (Z = 4)

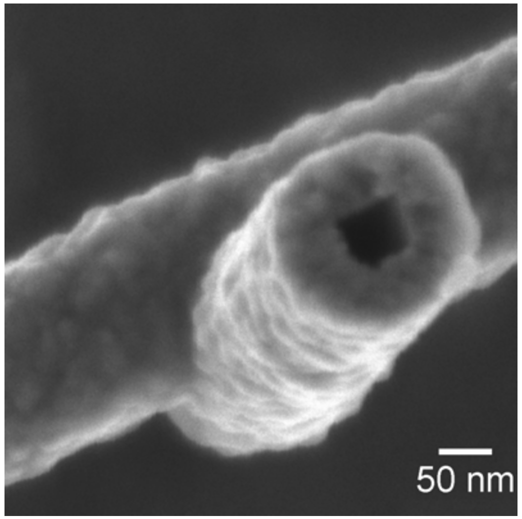
Auflösungsvermögen:
1,0 nm @ 15kV
2,2 nm @ 1kV
Beschleunigungsspannung:
0,5 - 30 kV

Feldemissions-Rasterelektronen-mikroskop (FE-REM)

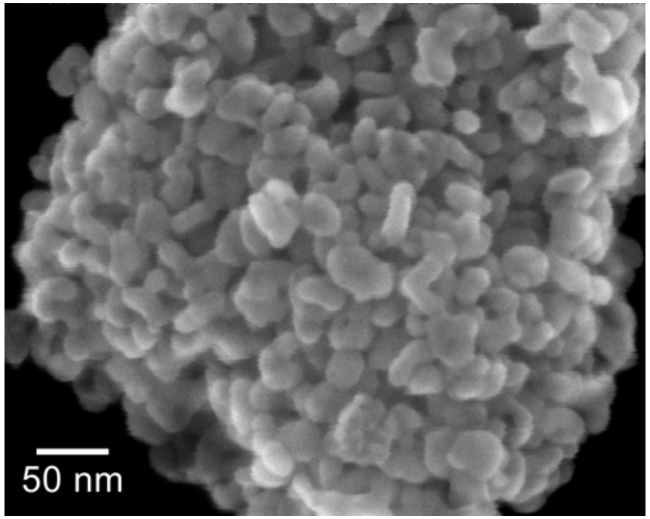
JEOL JSM-6700F



Bruchspiegel eines Perowskitrohrs (Membran zur Sauerstoffabtrennung)



Gekreuzte TiO_2-Hohlfasern



Katalysatorträger aus TiO_2 (Anatas)

- Transmissionselektronenmikroskopie (BF, DF, HRTEM)
- Raster-Transmissionselektronenmikroskopie (STEM mit BF, HAADF)
- Elektronenbeugung (SAED, CBED, auch energiegefiltert)
- Energiegefilterte Transmissionselektronenmikroskopie (EFTEM)
- Elektronen-Energieverlust-Spektroskopie (EELS, ELNES),

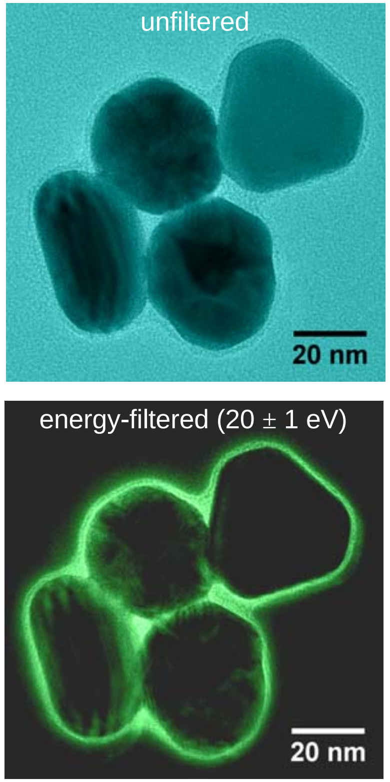
  Gatan Imaging Filter, GIF 2001, mit 1k-CCD-Kamera
- Energiedispersive Röntgenspektroskopie (EDXS),

  Oxford Instruments INCA 200, Detektion ab Be (Z = 4)

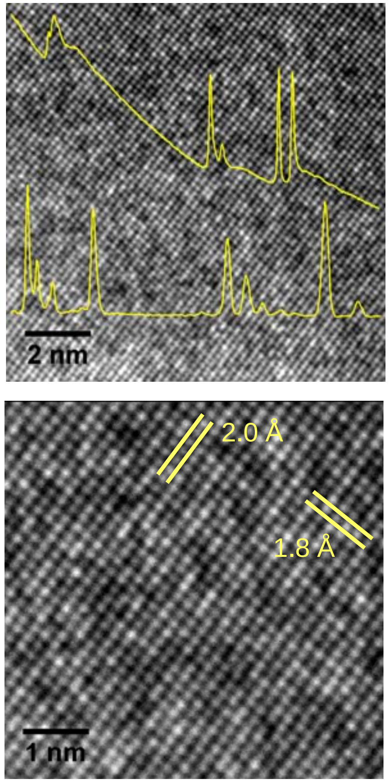
- Schottky-Feldemitter (ZrO/W(100))
- Beschleunigungsspannung: 200 kV (160 kV)
- Punktauflösung: ≤ 0,19 nm (C_s = 0,5 mm)
- Gitterauflösung für STEM: ≤ 0,2 nm
- Energieauflösung für EELS: ≤ 0,7 eV

Feldemissions-Transmissions-elektronenmikroskop (FE-TEM)

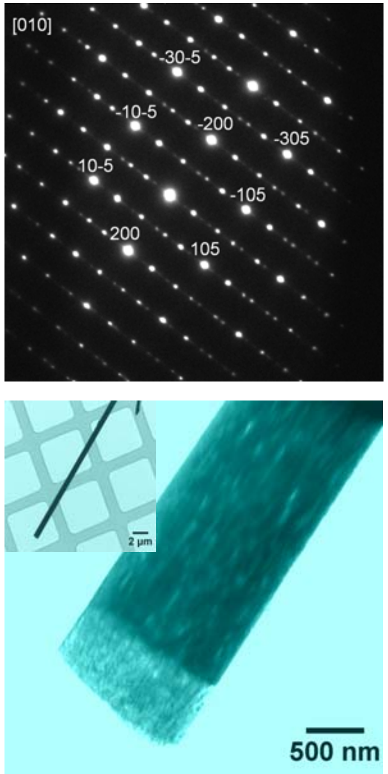
JEOL JEM-2100F-UHR



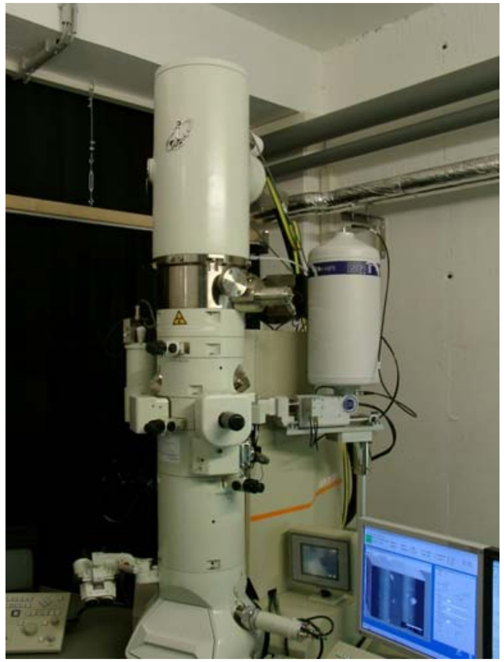
Goldteilchen, oberflächen-funktionalisiert mit Proteinfilm



Perowskit entlang [012] ($Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$)

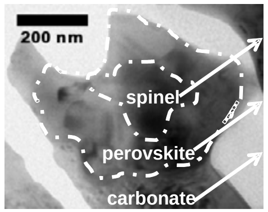


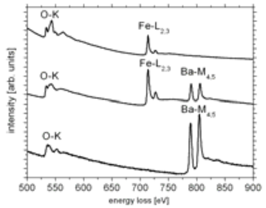
TiO_{2-x}-Stäbchen (Anatas) mit planaren Defekten

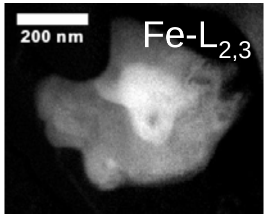


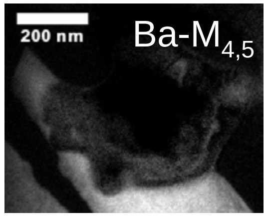
The sol-gel synthesis of perovskites involves nanoscale solid state reactions.

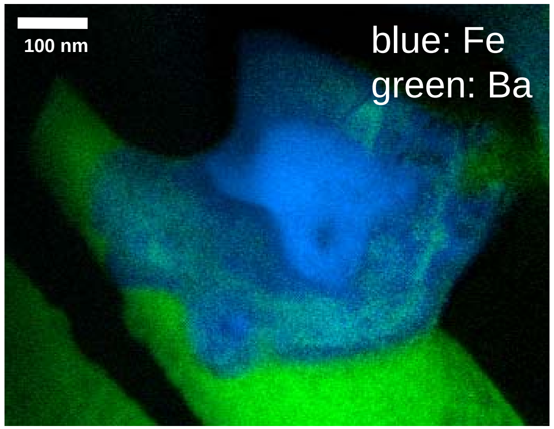
J. Martynczuk, M. Arnold,
H. Wang, J. Caro, A. Feldhoff,
Adv. Mater. (2007)





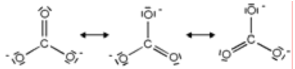


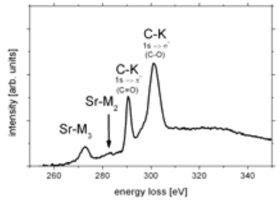


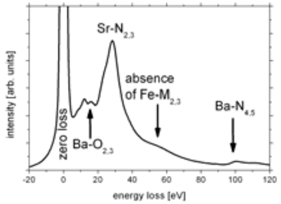


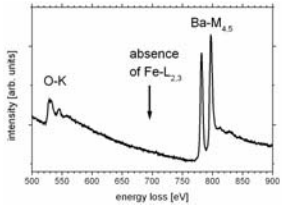
energy-filtered TEM

carbonate
$(Ba_{0.5}Sr_{0.5})CO_3$

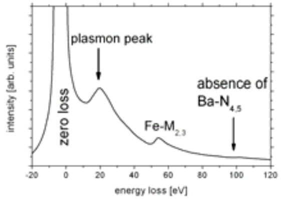


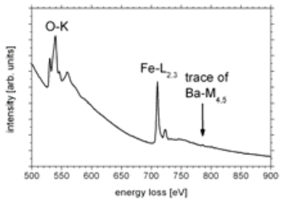




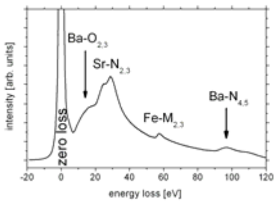


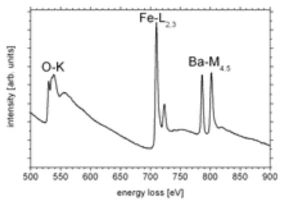
\+ spinel
$(Zn_{0.6}Fe_{0.4})Fe_2O_4$



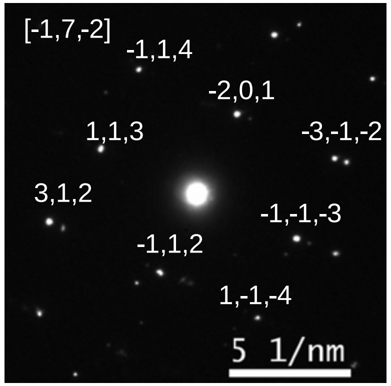


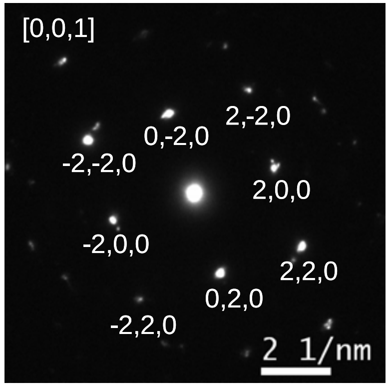
= perovskite
$(Ba_{0.5}Sr_{0.5})(Fe_{0.8}Zn_{0.2})O_3$

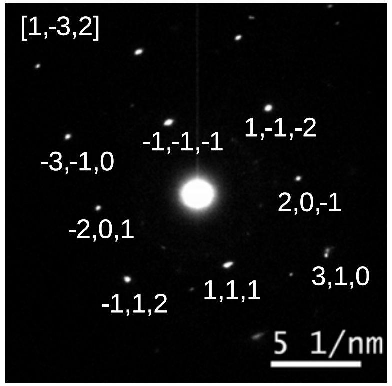




electron energy-loss spectroscopy







electron diffraction

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Prozesse an Festkörpern

Prof. Imbihl
Dynamische Prozesse
an Oberflächen

AK Becker, Lehrgebiet A

Beeinflussung der Kristallisation

von Halbleitern und Metallen

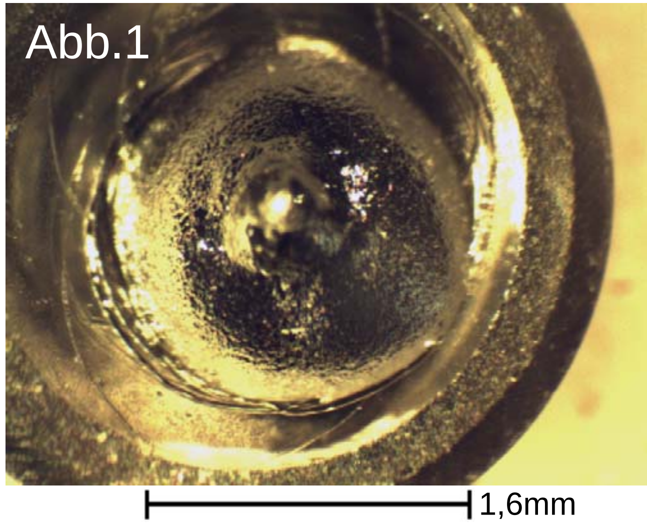
durch dispergierte Nanopartikel

z.B. Silizium und Nanopartikel z.B. Si_3N_4

Optische und NIR-Mikroskopie im Hochvakuum

Homogene Keimbildung

- reines Silizium ($T_{schmelz}$=1687K)
- Unterkühlung bis >100K möglich
- Einsetzen von homogener Keimbildung (Abb.2a-e)
- Schnelle Kristallisation (~1 sek)



Entstehung eines polykristallinen Probenkörpers mit rauer Oberfläche (Abb.1)

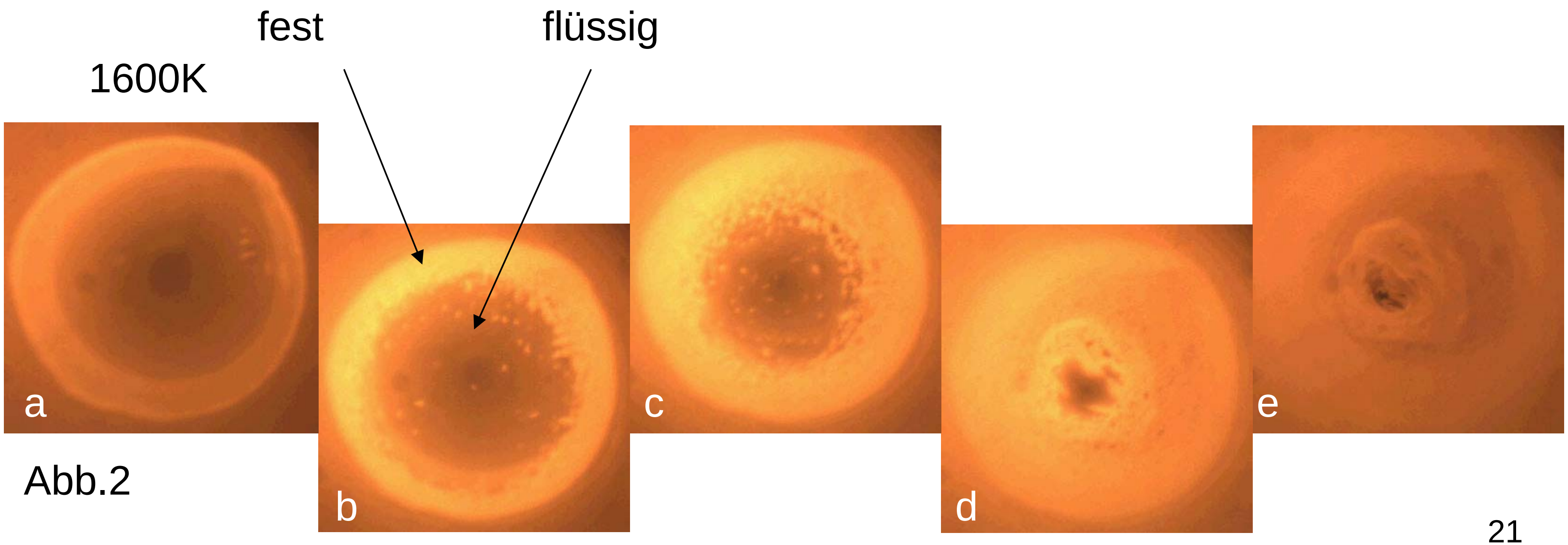


Abb.2

Heterogene Keimbildung

- Silizium mit Nanopartikeln <D>= 400nm
- geringe bis keine Unterkühlung möglich (<1K)
- Kristallisation ausgehend von heterogenen Keimen (Abb.4a-e)
- langsamere Kristallisation (~4-10 sek)

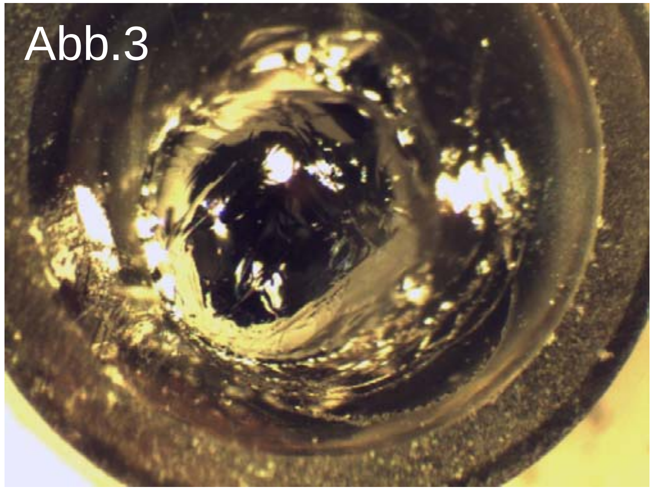


Abb.3

Probenkörper mit erkennbaren Kristalliten und glatter Oberfläche (Abb.3)

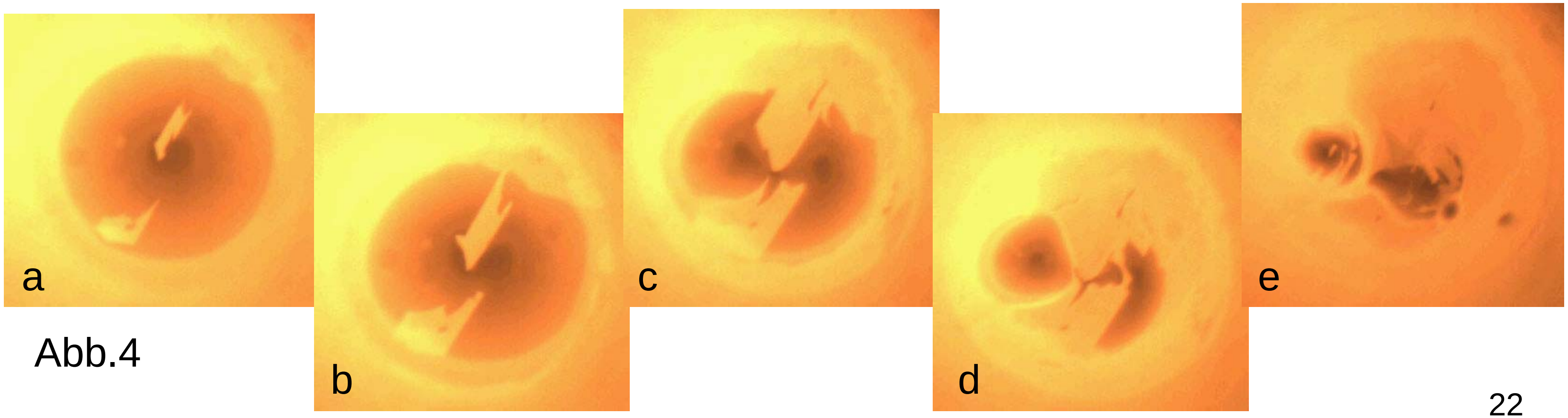


Abb.4

Dr. Jens-Uwe Grabow

- Überschallstrahl-Rotationspektroskopie:

Fourier Transform Microwave (FT-MW) Spectrometer

Experimentelle (Instrument) und Theoretische (QM) Entwicklungen

Produktion/Charakterisierung von größeren/instabilen Spezies:

Geometrische Struktur:	**Trägheitsmomente**
	(isotopologe Verschiebung → Koordinaten)
Interne Dynanik:	**Drehimpulskopplung**
	(Feinstruktur → Potentialbarrieren, Achsenlage, mehrdimensionale Tunnelpfade)
Elektronische Struktur:	**Kernspinkopplung**
	(Hyperfeinstruktur → molekulare Feldgradienten),
	Stark-Effekt
	(externes elektrisches Feld → Dipolmoment)

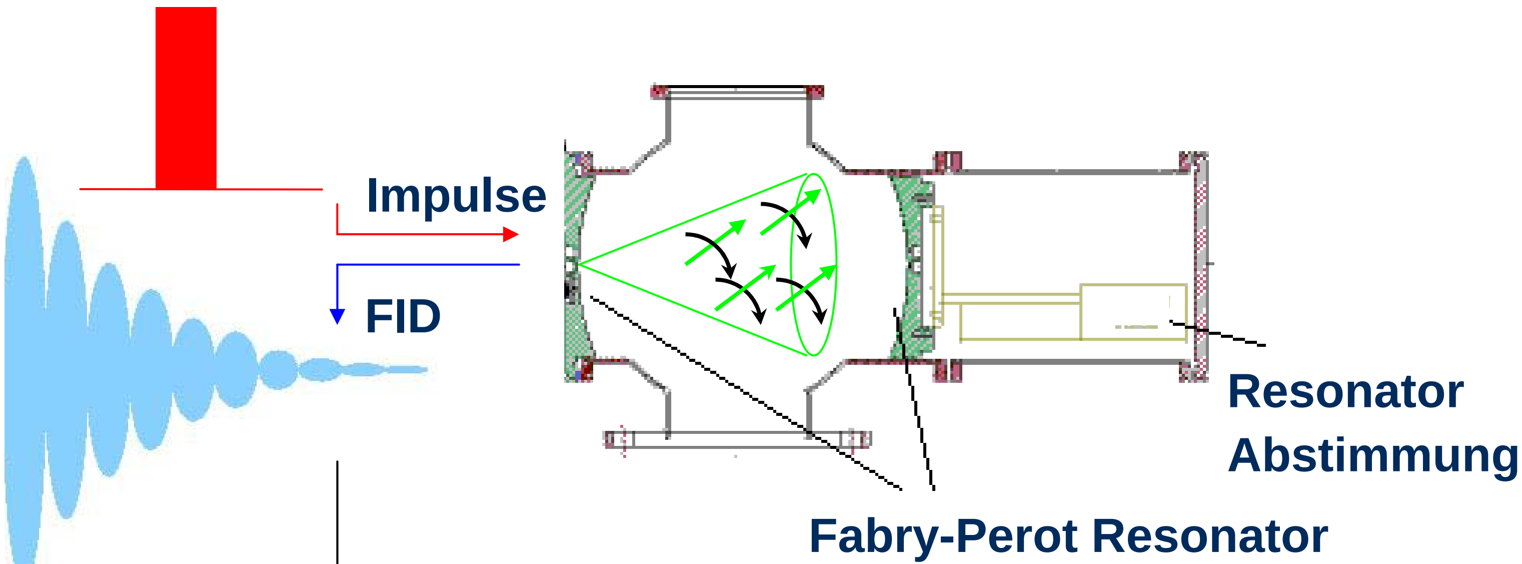
- **Hochdurchsatz-Experimente:**

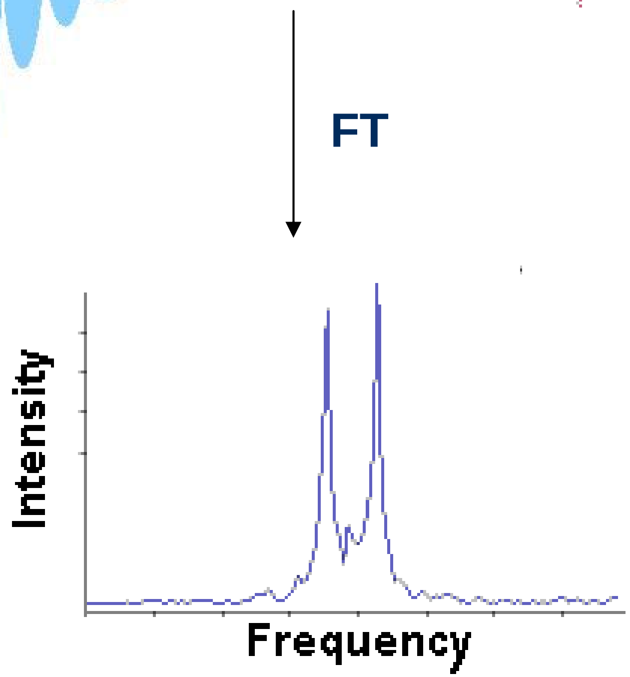
Scanning Probe Microwave (SP-MW) Microscope:

Experimentelle (Instrument) Entwicklungen:

Schnelle Charakterisierung der Eigenschaften dielektrischer Materialien

Molekularstrahl-Mikrowellen-Kohärenzspektroskopie





Polarizationspuls:

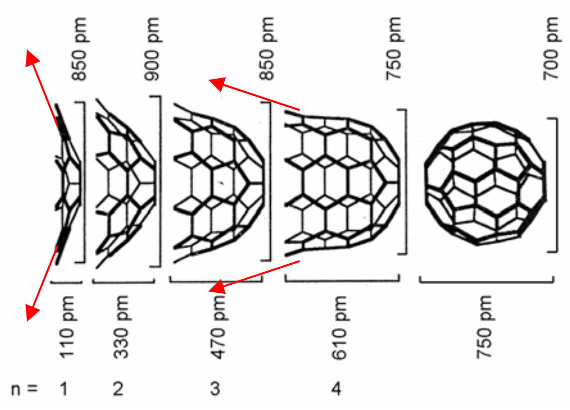
Kohärenz zwischen rotierenden molekularen Dipolen

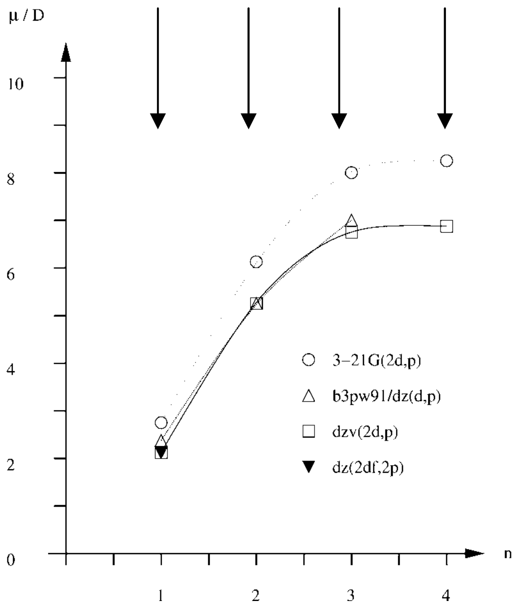
oszillierendes makroskopisches Dipolmoment:

Elektromagnetisches Feld mit Frequenzen der molekularen Übergänge

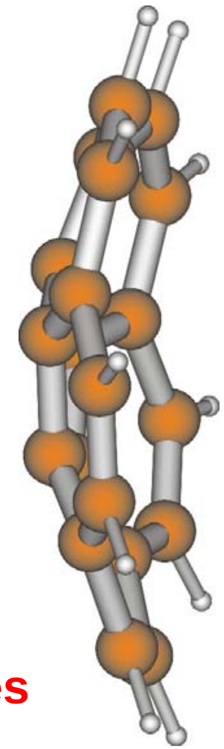
Dipolmoment von Corannulen

Dipolmomente von $C_{10(n+1)}H_{10}$





Spannung führt zu sehr substantiellen molekularen Dipolmomenten*



Experimentelles Dipolmoment (über Rotations-Stark-Effekt) :

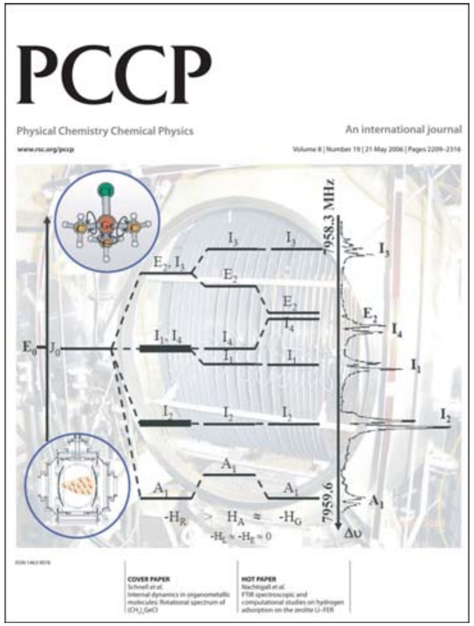
μ = 2.071(18) D

(= 6.908(60) 10^{-30} Cm)

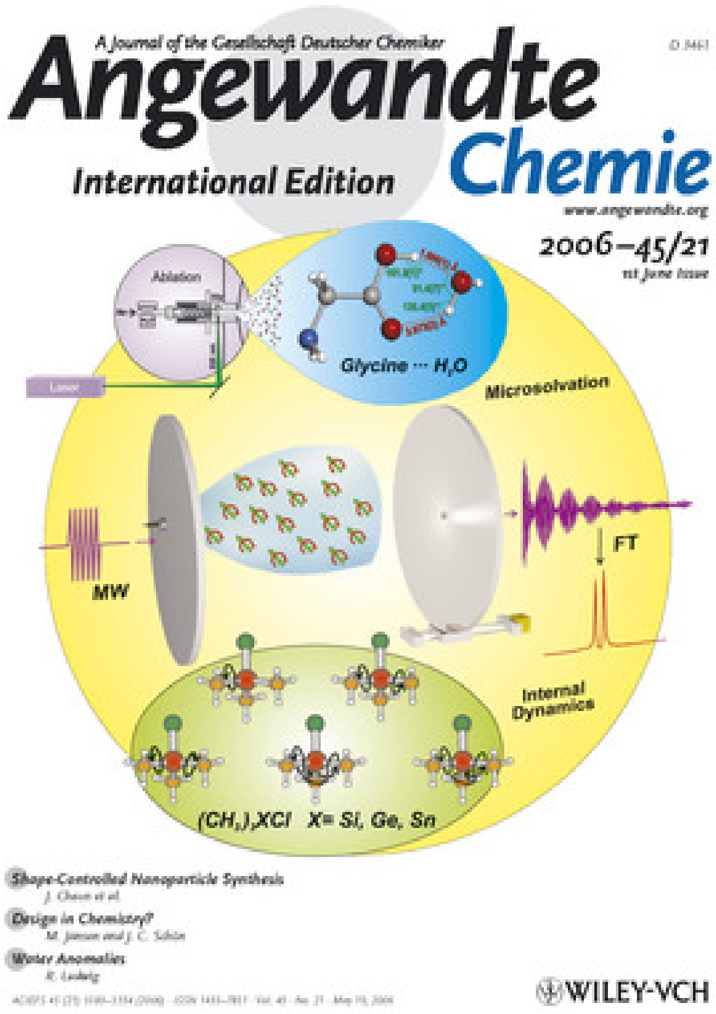
Größtes bekanntes Dipolmoment eines reinen, neutralen KW

*K.K. Baldridge, J.S. Siegel, *Theor. Chem. Acc.* **97**, 67-71 (1997).

Mehrdimensionale Tunnelpfade



M. Schnell, J.-U. Grabow, Phys.Chem.Chem.Phys. **8**, 2225(2006).



Molecular Dynamics

Multidimensional Large-Amplitude Motion: Revealing Concurrent Tunneling Pathways In Molecules With Several Internal Rotors**

*Melanie Schnell and Jens-Uwe Grabow**

Angew. Chem. Int. Ed. **2006**, 45, 3465-3470

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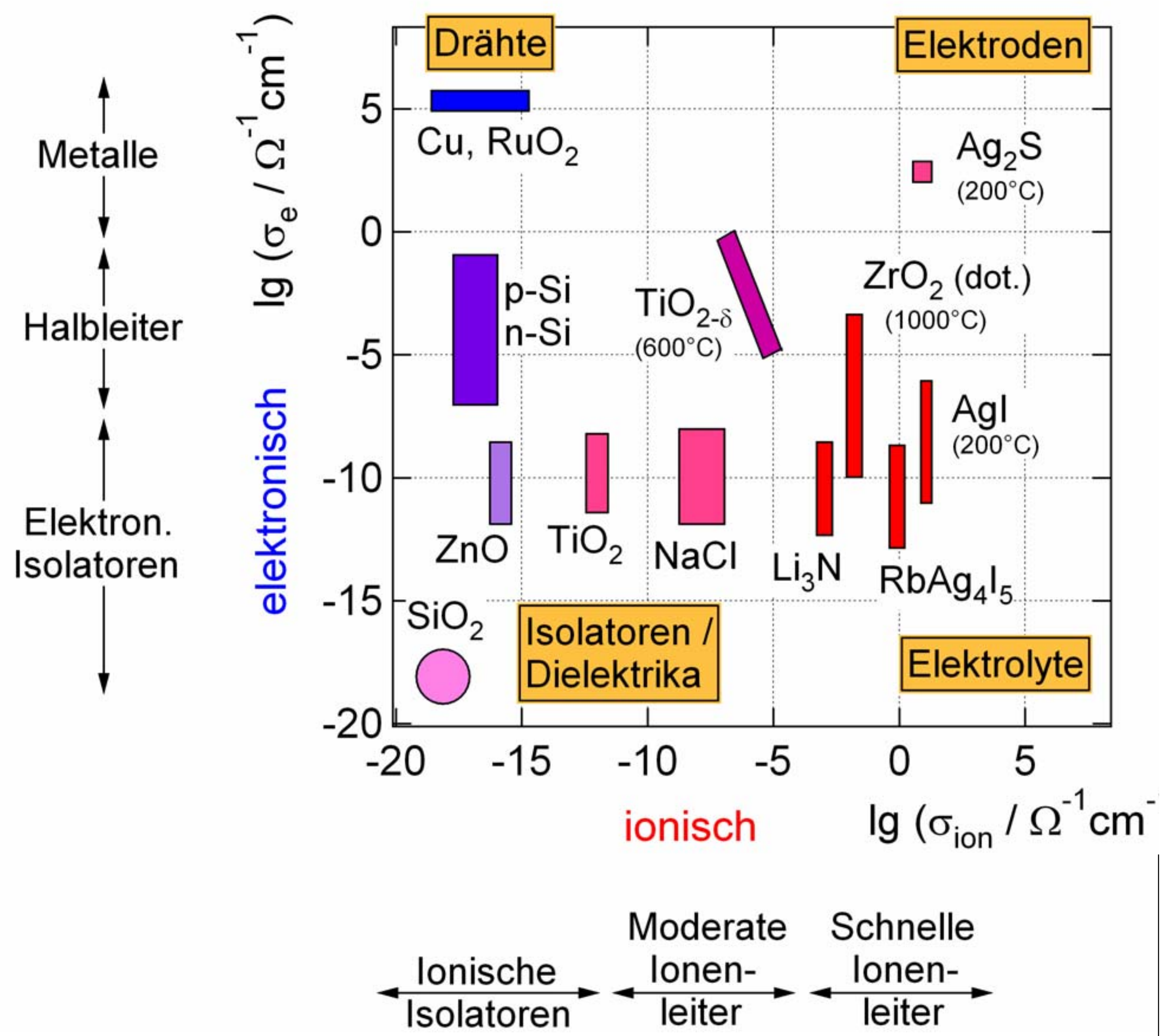
Dynamische und kinetische Prozesse in Festkörpern
- NMR-Spektroskopie
- Impedanz-Spektroskopie
- Mechanochemie

Prof. Imbihl
Dynamische Prozesse an Oberflächen

The forgotten dimension

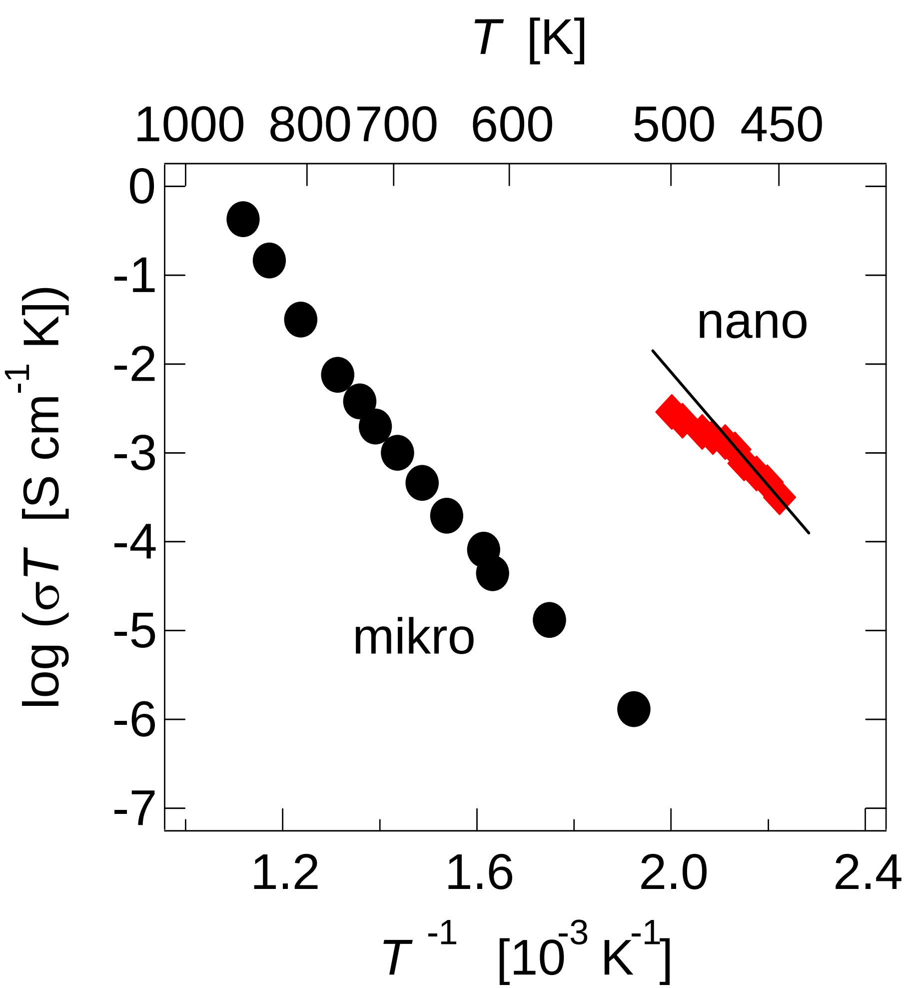
Nano-Engineering
=
Nano-Electronics
+ …
Nano-Ionics + ...



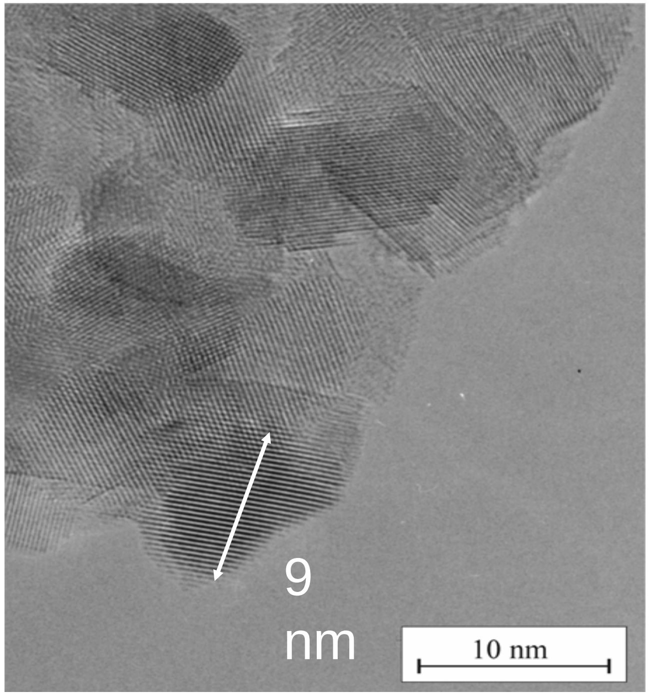
Elektrische Leitfähigkeit = elektronische und ionische

P. Heitjans, Sprecher Zentrum für Festkörperchemie und Neue Materialien (ZFM)
Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover

Nano-Ionics: F^- ion conductivity of nanocrystalline and microcrystalline CaF_2



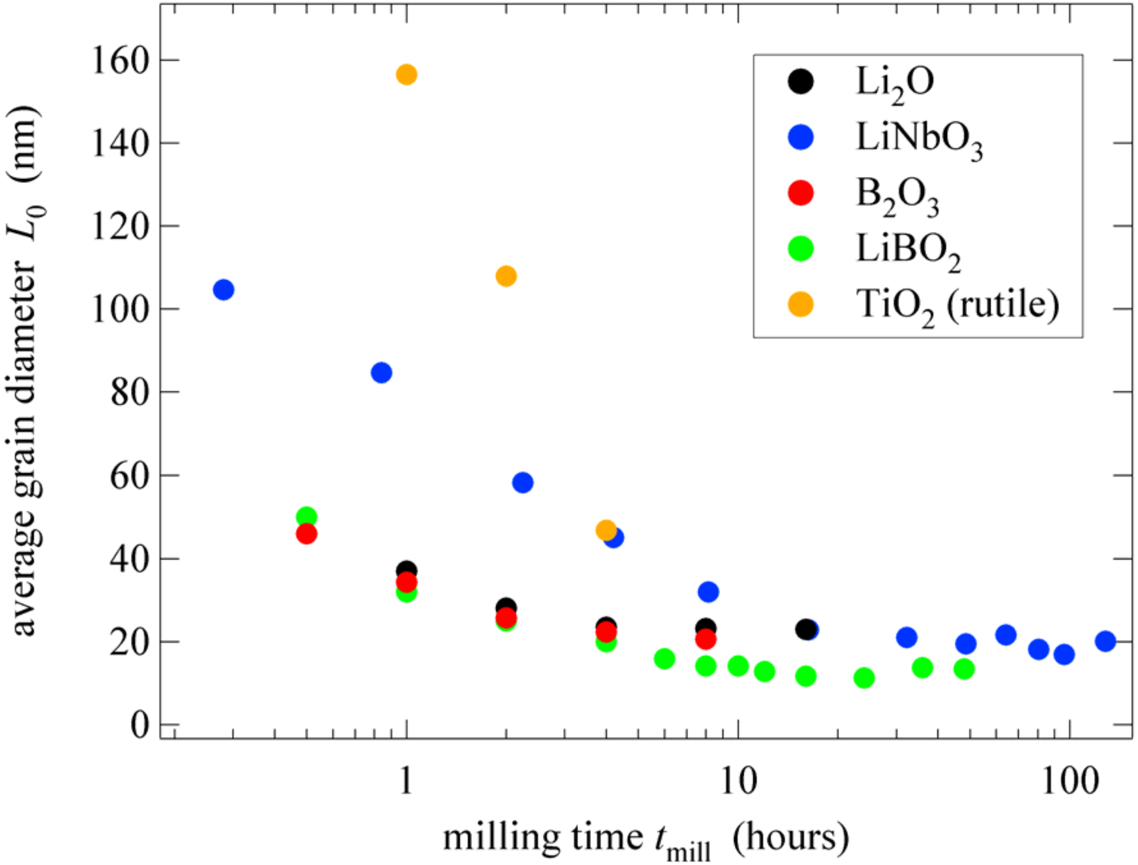
W. Puin, P. Heitjans et al.,
Solid State Ionics 131(2000)159

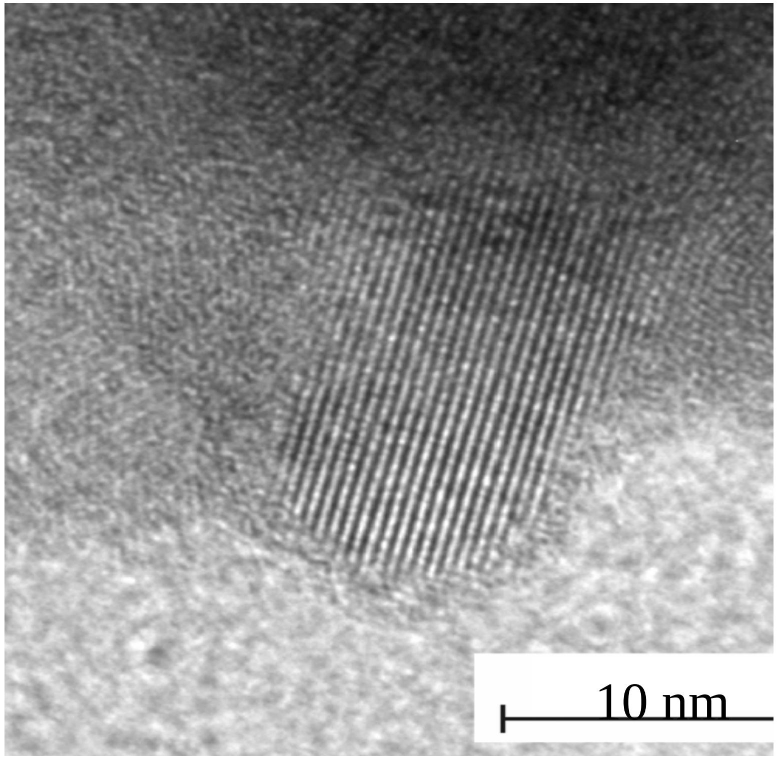


Nanokristallines CaF_2 besitzt um 4 GO höhere Leitfähigkeit

Abscheidung durch Edelgaskondensation

Into the nano range by ball milling

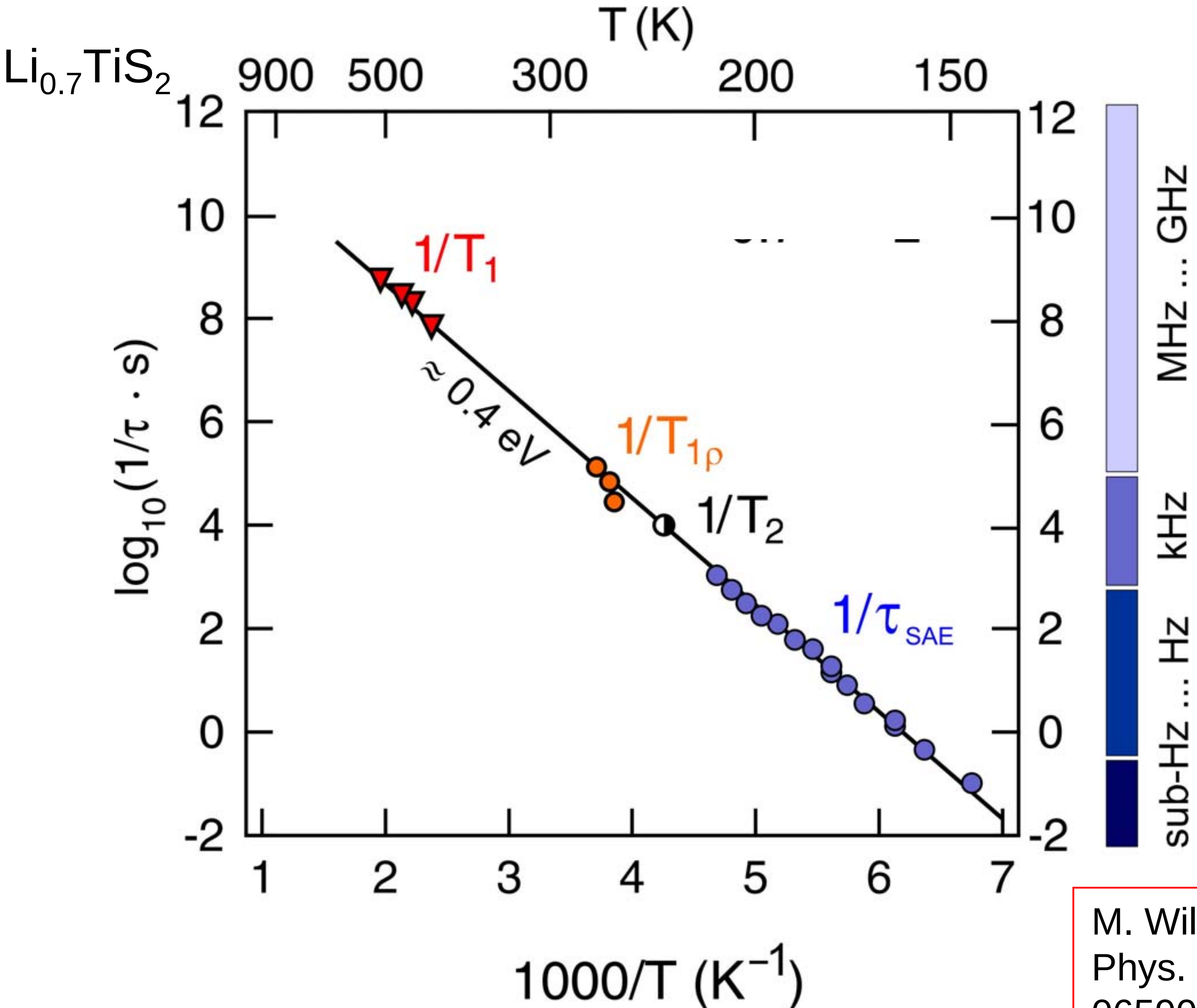




e.g. $LiNbO_3$

P. Heitjans, S. Indris,
J. Phys.: Condens. Matter
15 (2003) R1257

Motional correlation rates over 10 decades via NMR probing one single process



Nano-
sec

Dynamics

Deka-
sec

M. Wilkening, Heitjans et al.
Phys. Rev. Lett. 97 (2006)
065901

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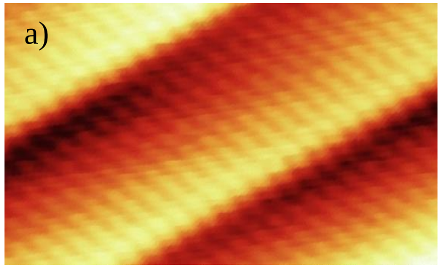
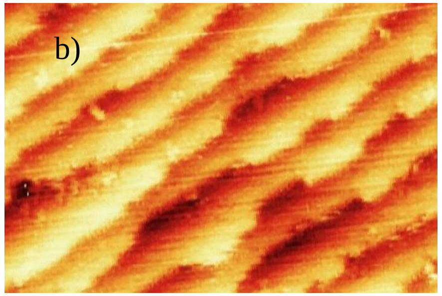
Prof. Imbihl
Dynamische Prozesse an Oberflächen. Surface Science

Surface Science: NH_3-Induced Step Meandering on Pt(443)

Restructuring by interaction NH_3 in catalysis (STM)





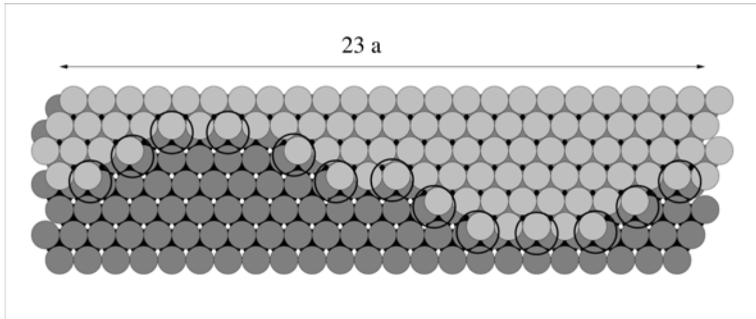
p_{NH3} = 1 x10^{-6} mbar

(a) clean surface

(b) 15 min

Imbihl

Creation of new step sites and with kink sites due to step meandering



Energy cost for restructuring ΔE_{Pt}:

$$J_{Pt} -_{Pt} = \frac{\Delta H_{sub}(Pt)}{12 N_A} = 47 kJ/mol$$

8 broken bonds (4 per row)

ΔE_{Pt} = 8 x 47 kJ/mol = 376 kJ/mol