SCIENCE ▪ PASSION ▪ TECHNOLOGY

SAXS applications in life science and material science using synchrotron radiation

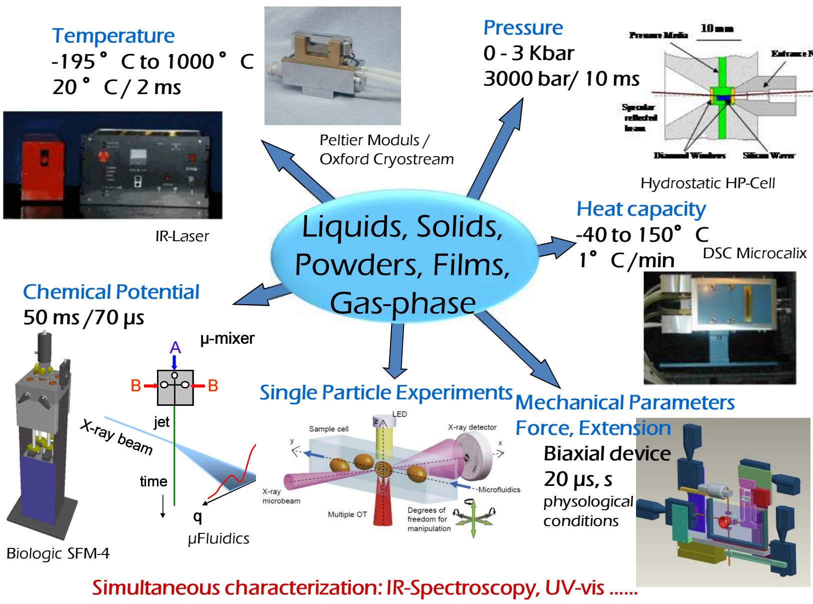
Heinz Amenitsch
TU-Graz & Austrian SAXS beamline, ELETTRA

Elettra Sincrotrone Trieste

Anorganische Chemie

Sample Environment

63



Simultaneous characterization: IR-Spectroscopy, UV-vis ……

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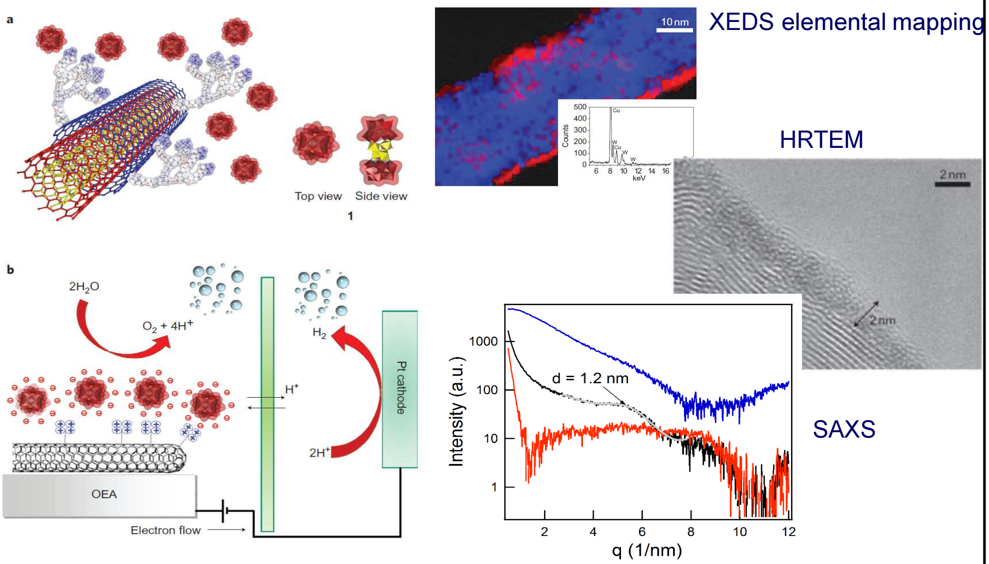
Anorganische Chemie

Characterization of carbon nanotube– polyoxometalate electrocatalytic interfaces

64

F.Toma, et al., Nature Chemistry, (2010), 10.1038/NCHEM.761



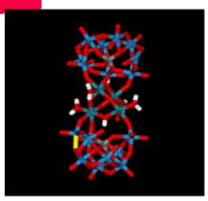
XEDS elemental mapping

HRTEM

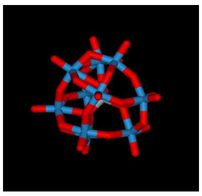
SAXS

Characterization of carbon nanotube– polyoxometalate electrocatalytic interfaces

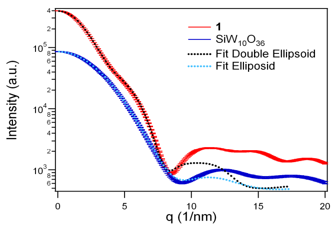
65



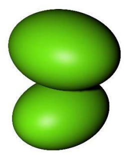
Ru4POM



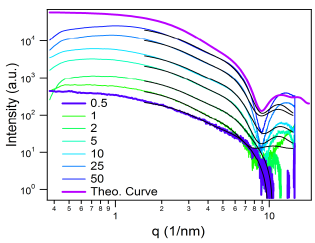
Precursor $SiW_{10}O_{36}$

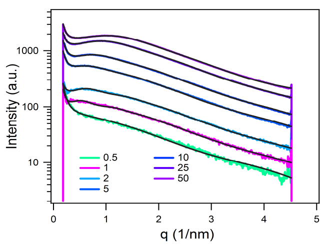


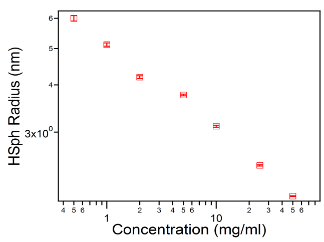
Simulation Crysol ATSAS D.Svergun



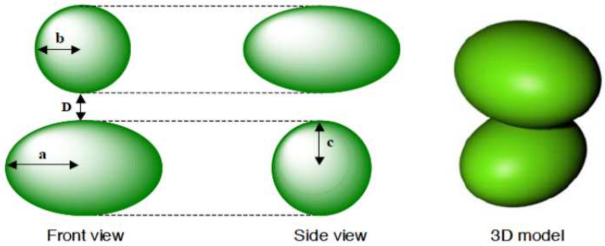
Double ellipsoid model







Institute of Chemistry, University of Graz, Austria



$$I_{scat} = I_0 \cdot \frac{1}{\pi} \int_0^{\pi} d\beta \int_0^{\pi/2} d\alpha \cdot \sin(\alpha) \cdot \frac{1}{4} \cdot F_{2ellip}(q,a,b,c,D,\alpha,\beta)^2 \qquad (1)$$

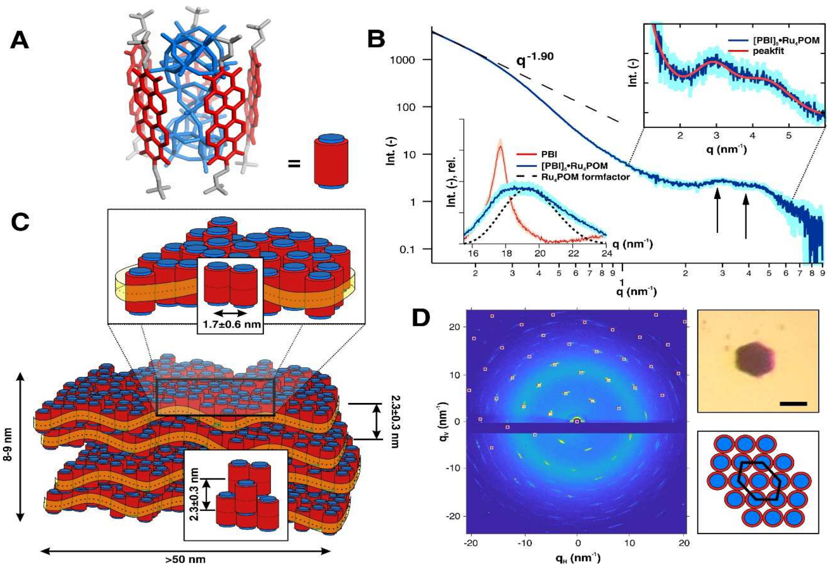
$$F_{2ellip}(q,a,b,c,R,\alpha,\beta)^2 = \left(F_{ellip}(R_1,q) + F_{ellip}(R_2,q)\right)^2 \cdot \cos\left(q \cdot (D/2 + c) \cdot \cos(\alpha)\right)^2 + \\ + \left(F_{ellip}(R_1,q) - F_{ellip}(R_2,q)\right)^2 \cdot \sin\left(q \cdot (D/2 + c) \cdot \cos(\alpha)\right)^2$$

$$F_{ellip}(R,q) = 3 \cdot \frac{\sin(q \cdot R) - q \cdot R \cdot \cos(q \cdot R)}{(q \cdot R)^3}$$

$$R_1 = \sqrt{\left(a^2 \cdot \sin(\beta)^2 + b^2 \cdot \cos(\beta)^2\right) \cdot \sin(\alpha)^2 + c^2 \cdot \cos(\alpha)^2}$$

$$R_2 = \sqrt{\left(b^2 \cdot \sin(\beta)^2 + a^2 \cdot \cos(\beta)^2\right) \cdot \sin(\alpha)^2 + c^2 \cdot \cos(\alpha)^2}$$

Artificial Quantasomes for Photo-assisted Water Oxidation



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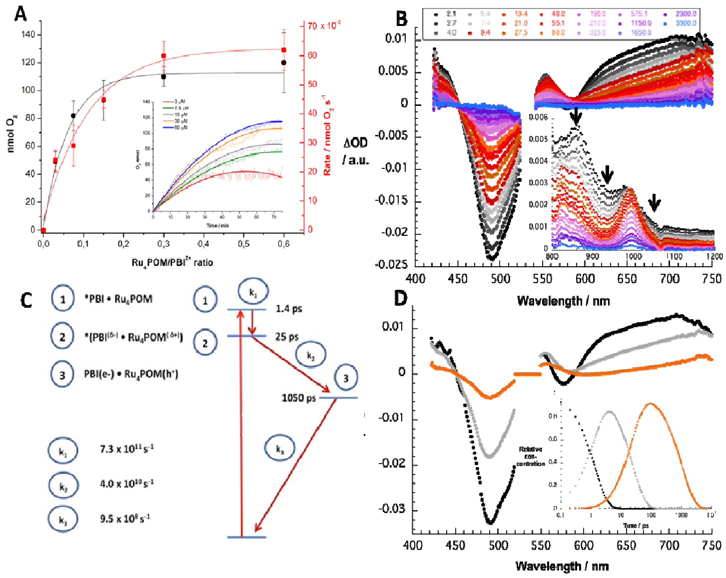
Anorganische CHEMIE

Artificial Quantasomes for Photo-assisted Water Oxidation

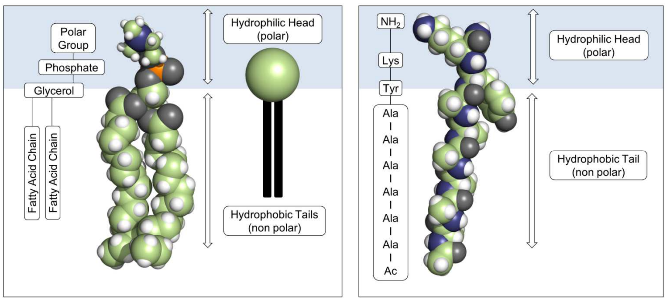
68



Marcella Bonchio,
Zois Syrgiannis,
Maurizio Prato et al.
Nature Chemistry
(2019)

Amphiphilic designer-peptides

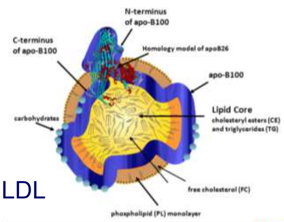
69

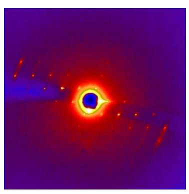


a phospholipid

an amphiphilic designer-peptide

a6yk

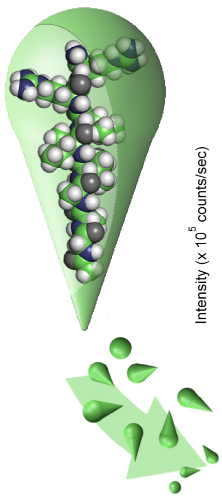




Gazit, E. *Chem. Soc. ReV.* **2007**
Cherny, I.; et al., *Angew. Chem., Int. Ed.* **2008**

LDL

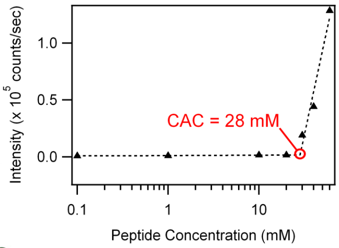
Self-assembly



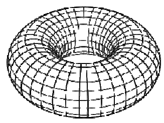
Spherical Micelles

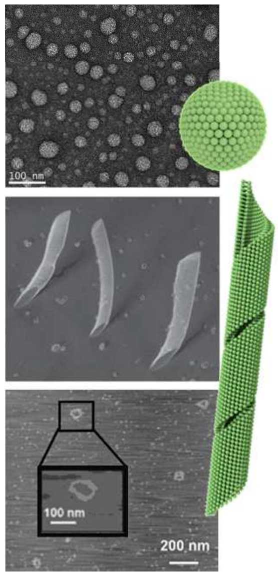
Vesicles

Bilayers



Self-Assembly





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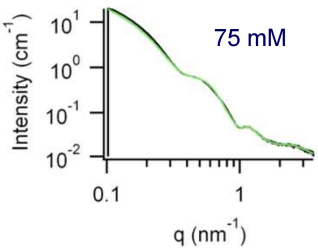
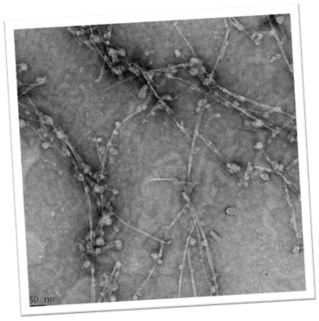
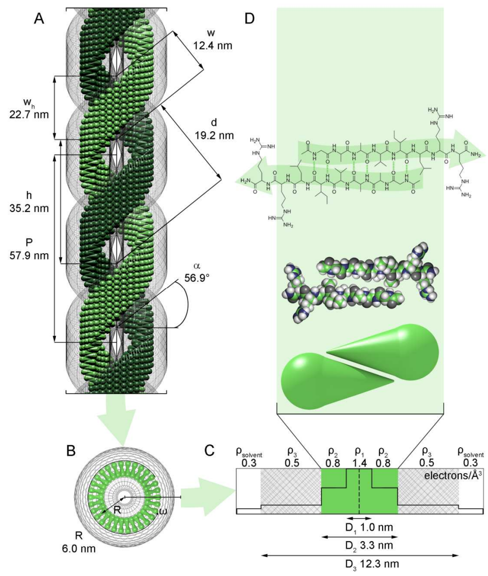
It's a double helix!







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The self-assembly process

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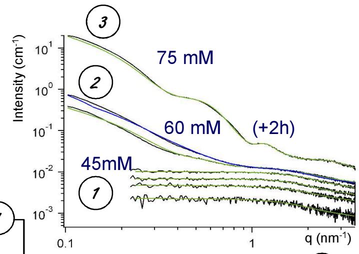
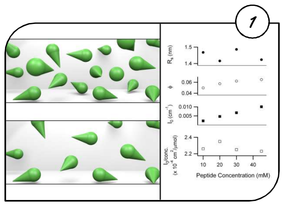
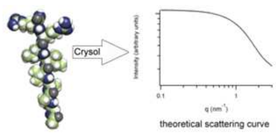
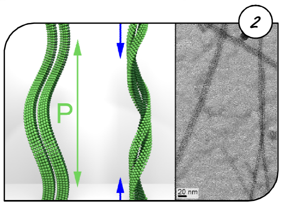


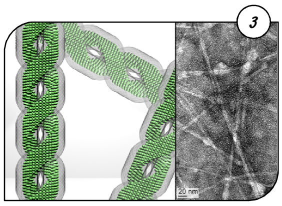


10-45 mM Monomers





60m M 3-layered single helical tape



75 mM 3-layered double helical tape

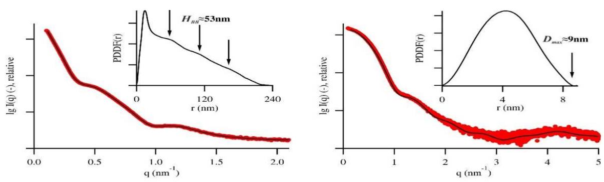
K.Kronmüller et al. sub to JACS (2013)

Pontoni D. et al., J. Chem, Phys, 2003
Svergun D.I. et al., J. Appl. Cryst., 1995

SAXS Software Development: SASHEL

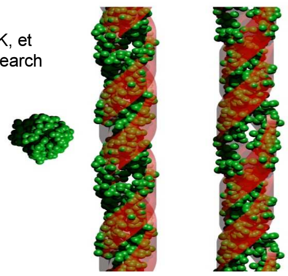
73

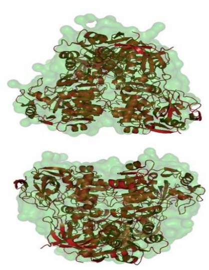
Ab initio modelling of elongated structures (and globular structures)



Alcohol Dehydrogenase 1
Valentini E et al., Nucleic Acids Res. **43** (2015)

Kornmueller,K, et al. NanoResearch (2018)

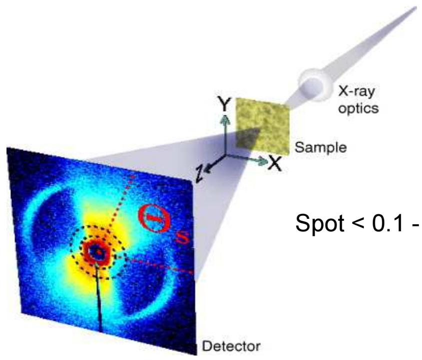




M. Burian , H.A. IUCrJ (2018)

Scanning SAXS - Biomaterials

74

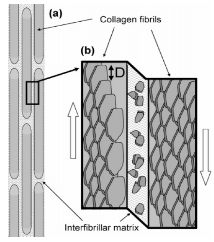


Spot < 0.1 -1 µm

Pic. O.Bunk, et al. New J. Phys. **11** (2009) 123016

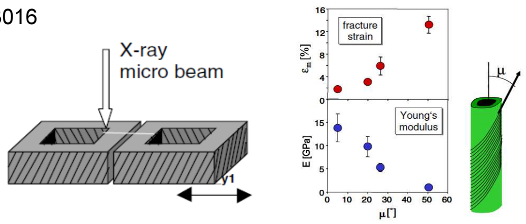
Bone

P.Fratzl



Wood

P.Fratzl



Silica-Sponges, Shells,
Tooth, Lobster, Worms,
Starch, Eyes……,

Scanning SAXS-Integral Parameters

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Integated Intensity

$$I = \int_{q\,min}^{q\,max} \int_{\chi_1}^{\chi_2} I(q,\chi) q^2 \; dq \; d\chi.$$

Porod Invariant

$$\tilde{I} = \int I(\mathbf{q}) \, d^3 q = \int_0^\infty q^2 \; dq \int_0^\pi \sin\psi \; d\psi \int_0^{2\pi} I(q,\psi,\chi) \; d\chi$$
$$= 2\pi^2 \varphi_1 \varphi_2 (\Delta\rho)^2,$$

T-Parameter

$$T = \frac{4}{\pi P} \int_0^\infty I(q) q^2 \; dq = 4 \frac{\varphi_1 \varphi_2}{\sigma}$$

Porod (1951,1952)

Scanning SAXS - Orientation

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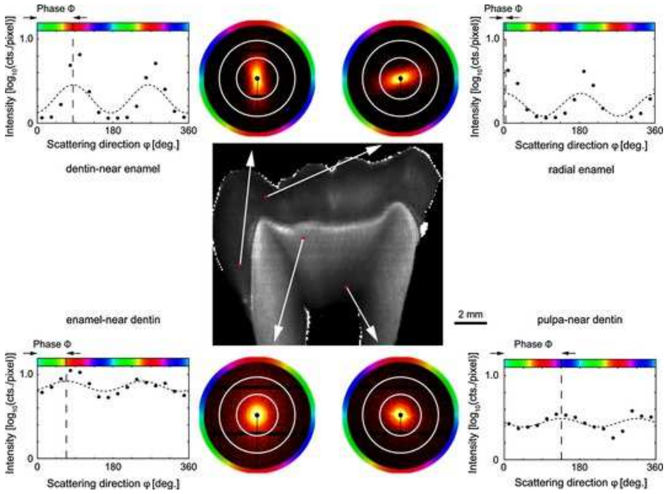
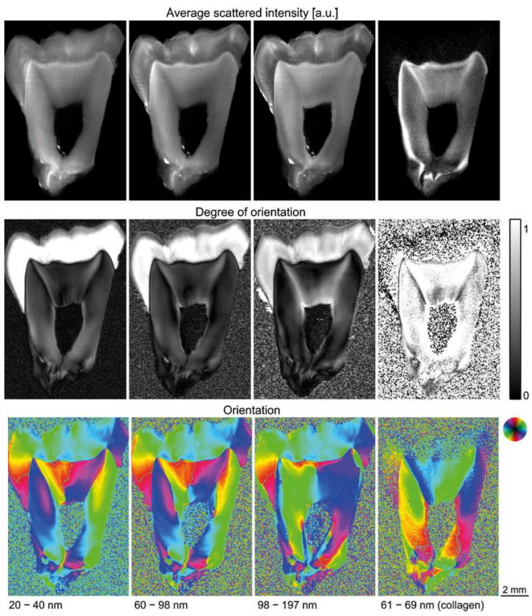


Geiser S. et al., Biointerphases
Journal for the Quantitative Biological Interface Data, 2012

Scanning SAXS - Tooth

77



Liposomes and SAXS

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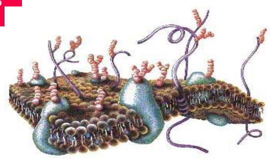
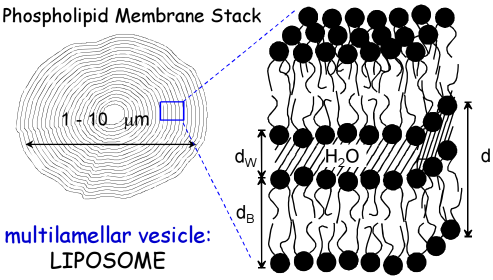


The boundaries of cells are formed by biological membranes, the barriers that define the inside and the outside of a cell.

Phospholipids are the major components of biological membranes that form the structural matrix into which proteins are imbedded.

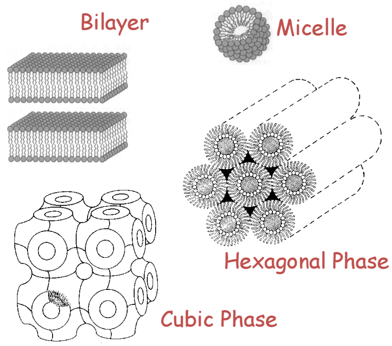
In aqueous solution:
self assembly into, e.g.,
unilamellar vesicles

Phospholipid Membrane Stack



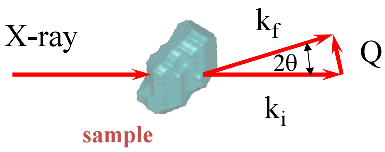
multilamellar vesicle:
LIPOSOME

Lyotropic Phases

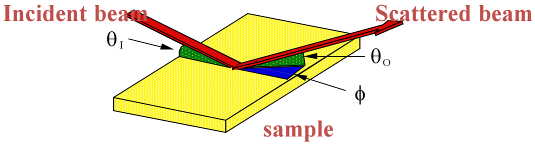


Small Angle Scattering - Surface Diffraction

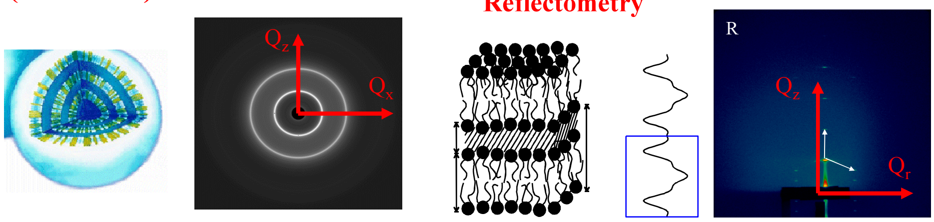
79



Small-Angle Scattering (Diffraction)



Grazing Incidence Small-Angle Scattering (GISAS) + Reflectometry



$$I(Q) = \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle \qquad I(Q_z, Q_r) = \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle_r$$

Distorted Wave Born Approximation

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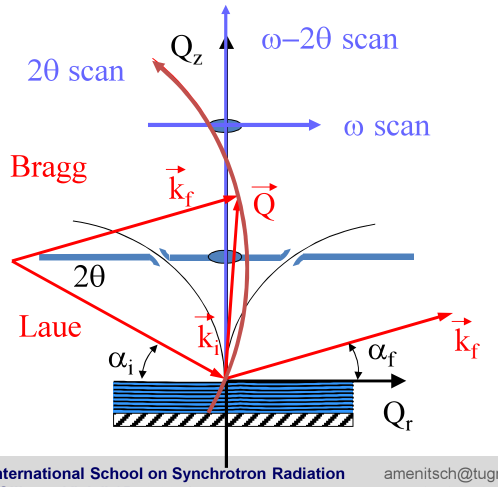
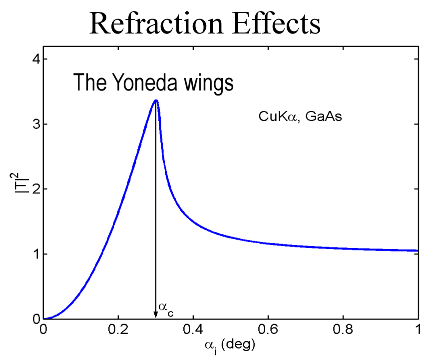
Vineyard (1982), Shinha et.al. (1988)

$$I(Q_z,Q_r) = |T_i(\alpha_i)|^2 \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle_r |T_f(\alpha_f)|^2$$





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„Higher Orders" of DWBA

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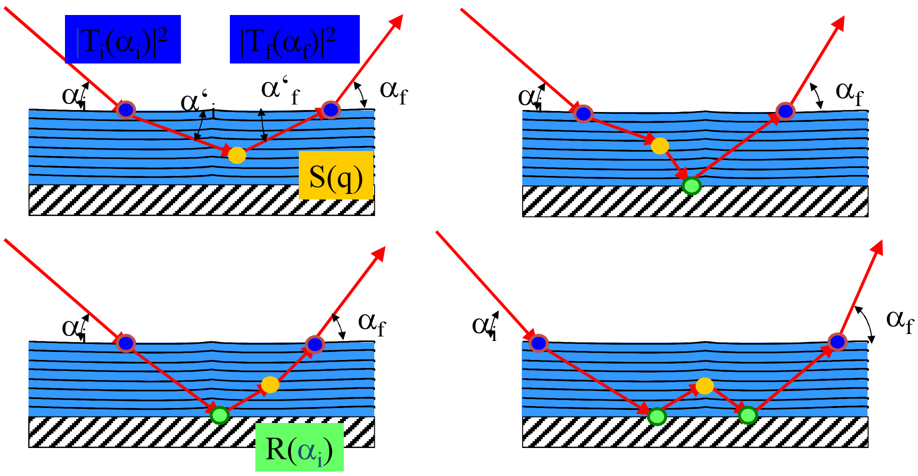

Lazzari R, ISGISAXS: program, J APPL CRYSTALLOGR 35: 406, (2002)

http://www.esrf.fr/computing/scientific/joint_projects/IsGISAXS/isgisaxs.htm

M.P.Tate et al., J.Phys.Chem, 2006

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Distorted Wave Born Approximation

82

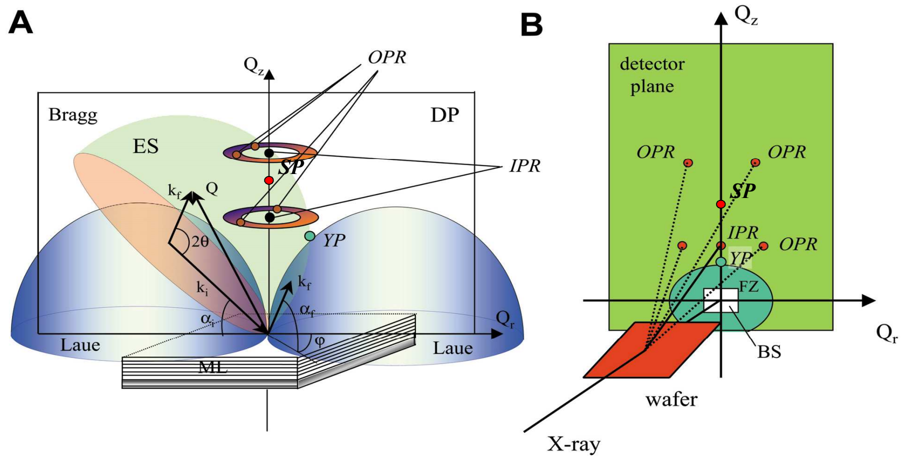
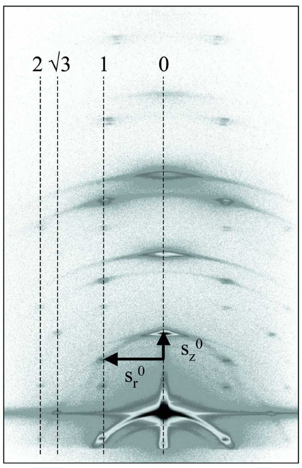
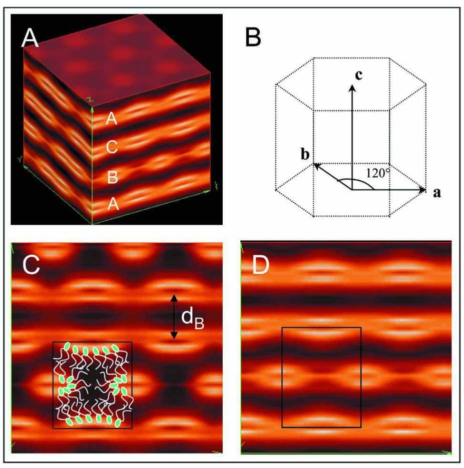


Fig. (A) the scattering geometry in reciprocal space. (B) Scattering geometry in real space. The abbreviations are: (ES) Ewald sphere, (DP) diffraction plane, (OPR) out-of plane reflections, (IPR) in-plane reflections, (ML) multi-layer, (FZ) forbidden zone, (BS) beam stop.

Surface Diffraction Lipids – Rhombohedral Phase

83





Diffraction Pattern DOPC @ 25° C, 35% rel. humidity

Electron Density Reconstruction: -C DPhPC (d_B= 44.3 Å) -D DOPC (d_B= 48.7 Å), but a= 67 Å / 68 Å

Rappolt,M, et.al., Adv. Coll. and Interf. Science, 111 (2004)   L. Yang, H.W. Huang, Biophys. J. 84 (2003)

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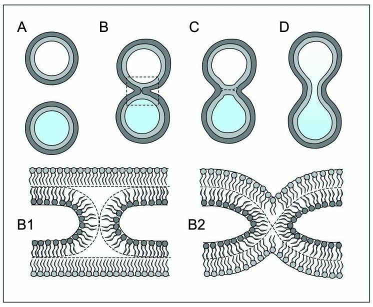
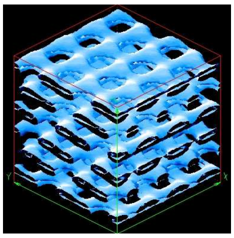
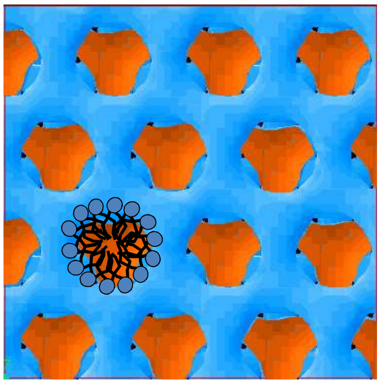
What do we learn? Membrane Fusion

84







The radius of the torus seems to be confined by the head-group size…

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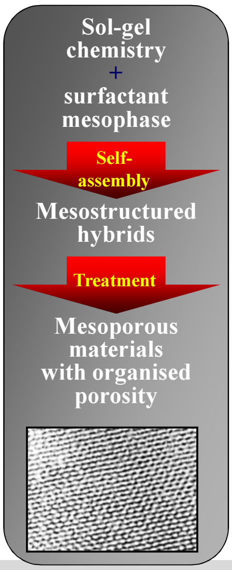
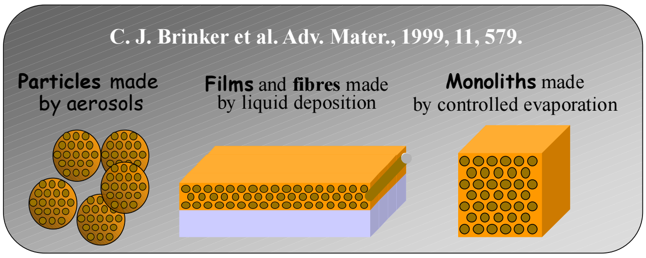
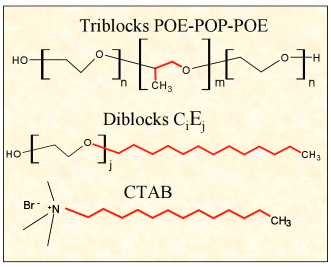
Surface diffraction: Formation of aligned mesoporous thin films

85







SiO_2 : $Si(OR)_4$
TiO_2 : $TiCl_4$ - $Ti(OR)_4$
ZrO_2 : $ZrCl_4$ - $Zr(OR)_4$
Al_2O_3 : $AlCl_3$
VO_{2-x} : $VOCl_3$
Y_2O_3 : YCl_3
Nb_2O_5 : $NbCl_5$
And binaries systems

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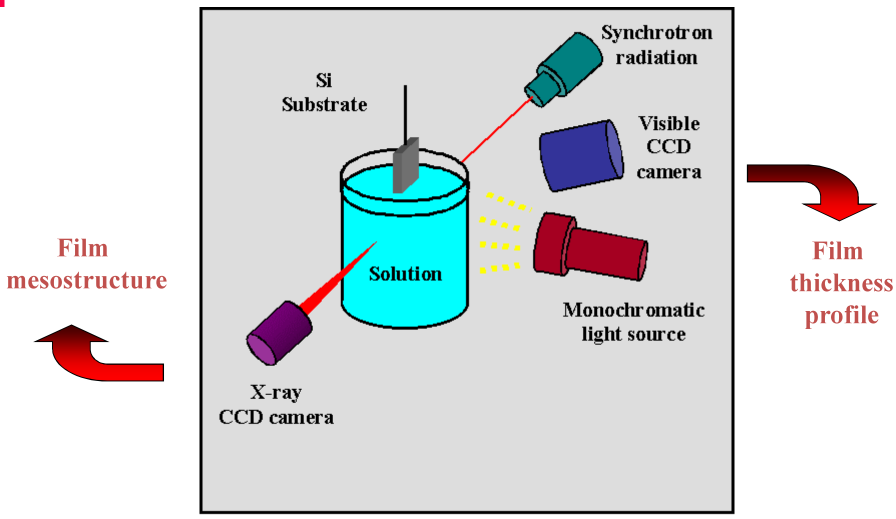
amenitsch@elettra.trieste.it

The Self-Assembly of thin films as seen by In- Situ SAXS and interferometry

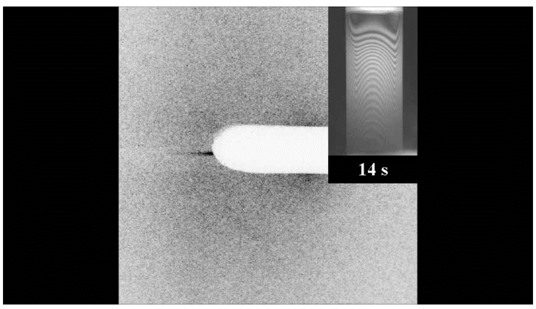
86

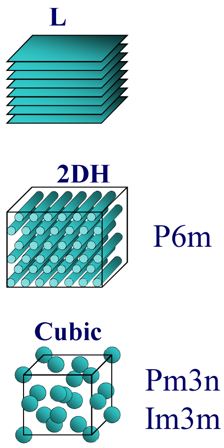


Surface diffraction: Formation of aligned mesoporous thin films

87

CTAB / Si = 0,18
H_2O / Si = 5
HCl / Si = 0.15
Ageing time
Relative Humidity

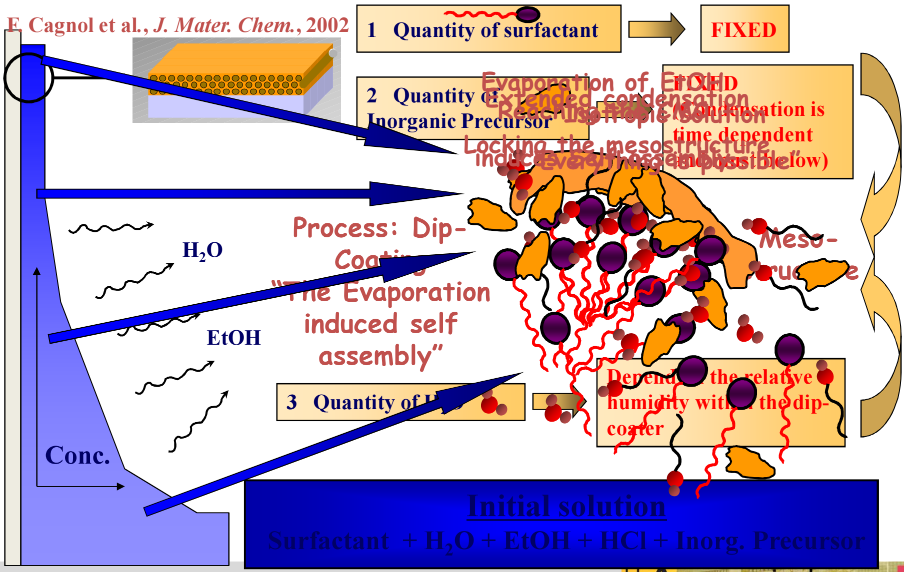




Grosso D, et.al., CHEMISTRY OF MATERIALS *14*, 931,(2002)

The Modulable Steady State

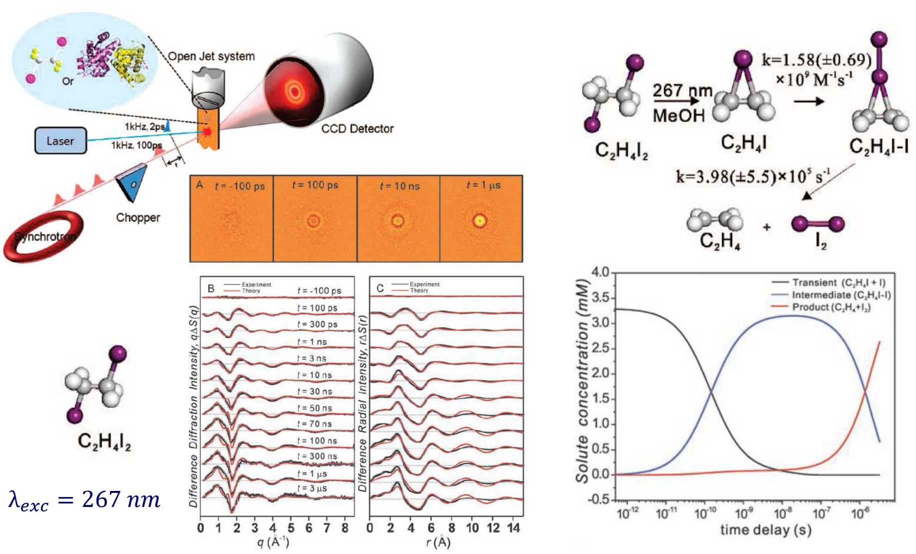
88



Pump Probe: Transient solution scattering

89

Taken from: H.Ihee, et.al. Science **309**, 1233 (2005).



Pump Probe: Implementation

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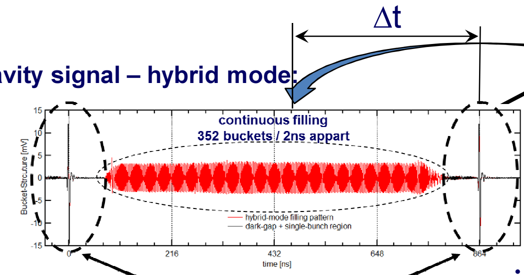
Elettra storage ring specifications

- 80 ps x-ray pulses
- 500 MHz cavity -> one pulse every 2ns
- 432 bucket slots -> 864ns circumference time

Cavity signal – hybrid mode:



160ns dark gap + single bunch

Pharos 20W Nd YAG:Laser

- Pulse width < 230 fs
- Wavelength Harmonics of 1030nm
- Chose-able repetition rate up to 600 kHz
- 100µJ pulses (@1030nm)
- Time-jitter < 5ps

(End September 2018)

Pump Probe

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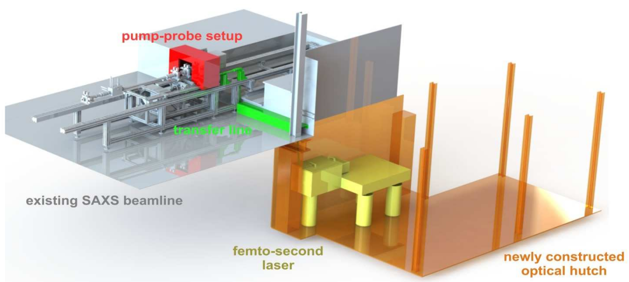

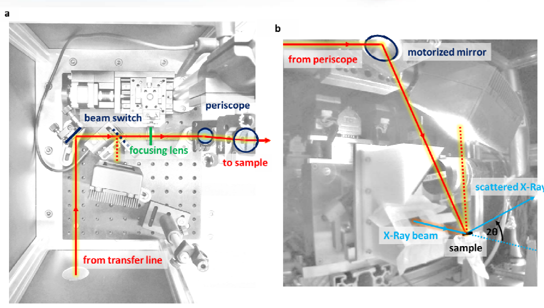

Pump Probe

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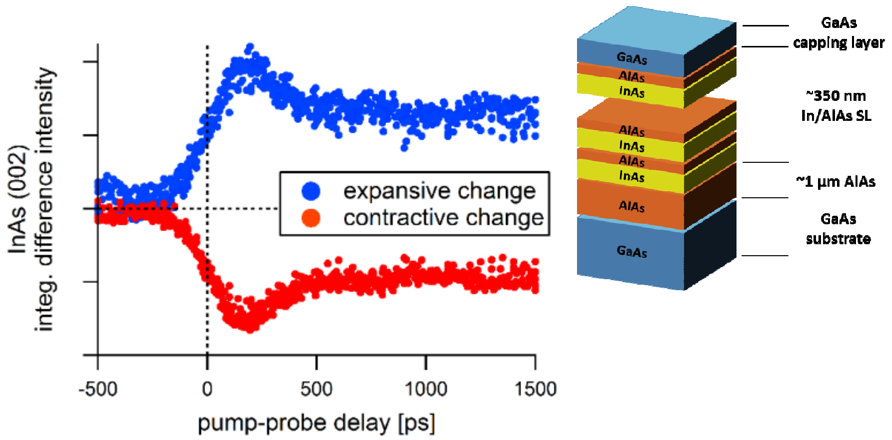
Transient heat-transfer



M. Burian, B. Marmiroli, A. Radeticchio, C. Morello, D. Naumenko, G. Biasiol, H. Amenitsch. (2020) J.Appl.Cryst.

Electrochemistry - GISAXS

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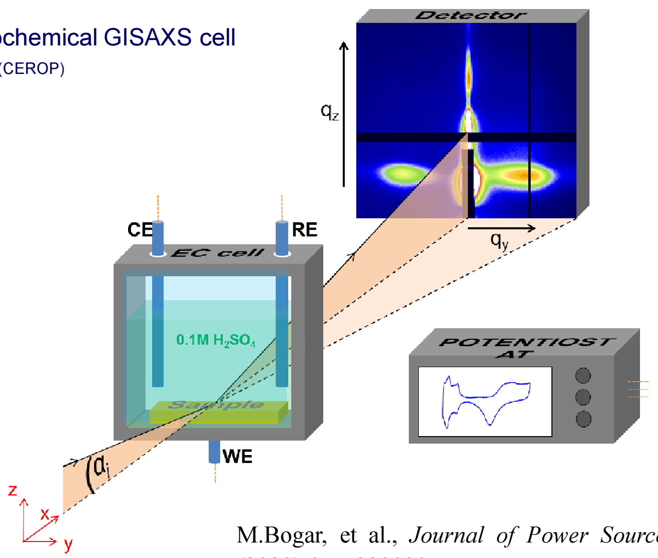
-Electrochemical GISAXS cell

M.Bogar (CEROP)
P.Wieser



M.Bogar, et al., *Journal of Power Sources* (2020) 477, 229030.

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GISAXS: Pt/Ni nanocatalyst fuel cell

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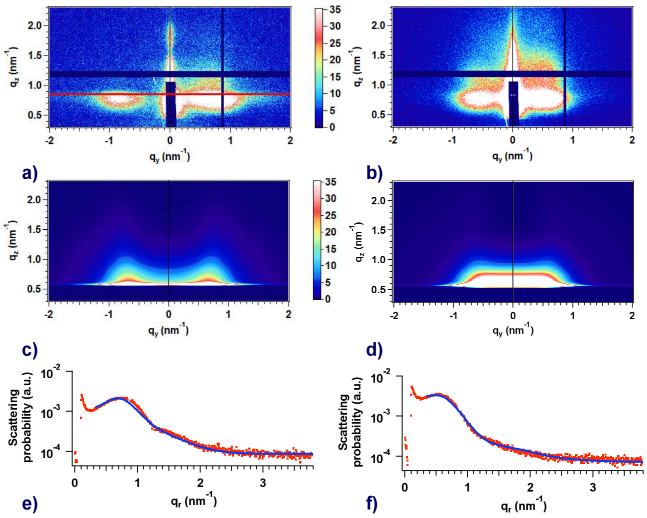

LAYER GEOMETRY:
sandwiched islands

FORM FACTOR:
random spheroid,
H/D constant

SIZE DISTRIBUTION:
Log Norm

STUCTURE FACTOR:
Perkus-Yevick

FORM FACTOR:
D: 4.3 nm
FWHM: 3.7 nm
H/D: 5

STRUCTURE FACTOR:
A/D: 2.95
eta: 0.127

FITGISAXS - D. Babonneau, J.Appl.Cryst, (2010)

GISAXS: Pt/Ni nanocatalyst fuel cell

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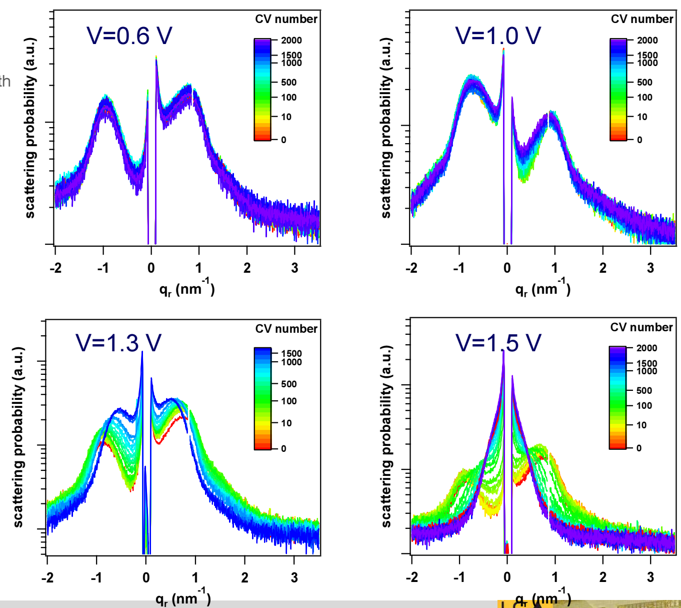
CV# 0 – 1500th



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Sketch of the Model - GISAXS: Pt/Ni nanocatalyst

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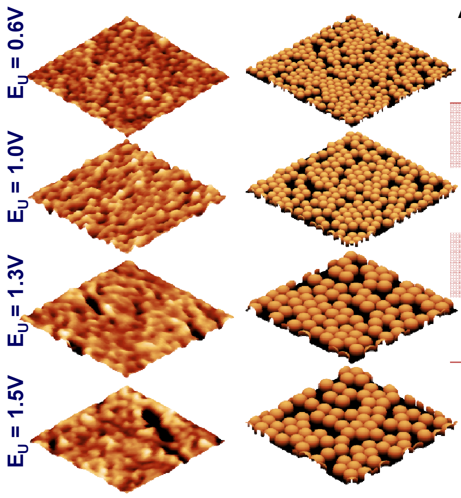

ΔV (V)	R_P (nm)	σ_P (nm)	D_{IP} (nm)
0.6	1.61 ± 0.14	0.56 ± 0.01	6.54 ± 0.04
1.0	1.77 ± 0.06	0.69 ± 0.03	6.50 ± 0.04
1.3	2.52 ± 0.14	0.84 ± 0.06	8.14 ± 0.06
1.5	2.64 ± 0.54	1.55 ± 0.06	14.54 ± 0.06

I. Khalakhan, et al., *ACS Applied Materials and Interfaces* (2020) 12, 17602.

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Anorganische Chemie

Pt_xNi_{1-x} Dependence - GISAXS: Pt/Ni nanocatalyst

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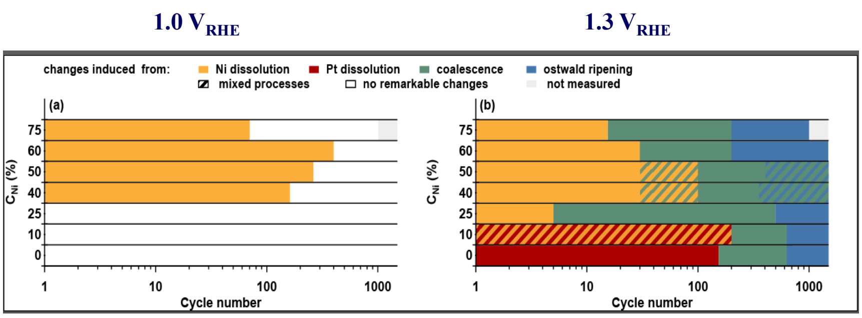

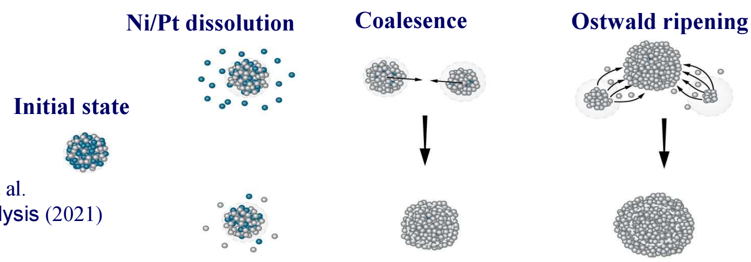

M.Bogar et al.
ACS Catalysis (2021)

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PART I:

-Introduction to the Theory (“Graz School’

-From Experiments to Real Space

PART II:

-Bio-SAXS (“Hamburg School”)

-Examples: -Chemistry
-Hierarchical Materials

-Gracing Incidence SAXS (“no school”)
-Biomembranes
-*In situ* Chemistry
- *Pump-Probe*
- *In operando Electrochemistry*

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SAXS on the beach

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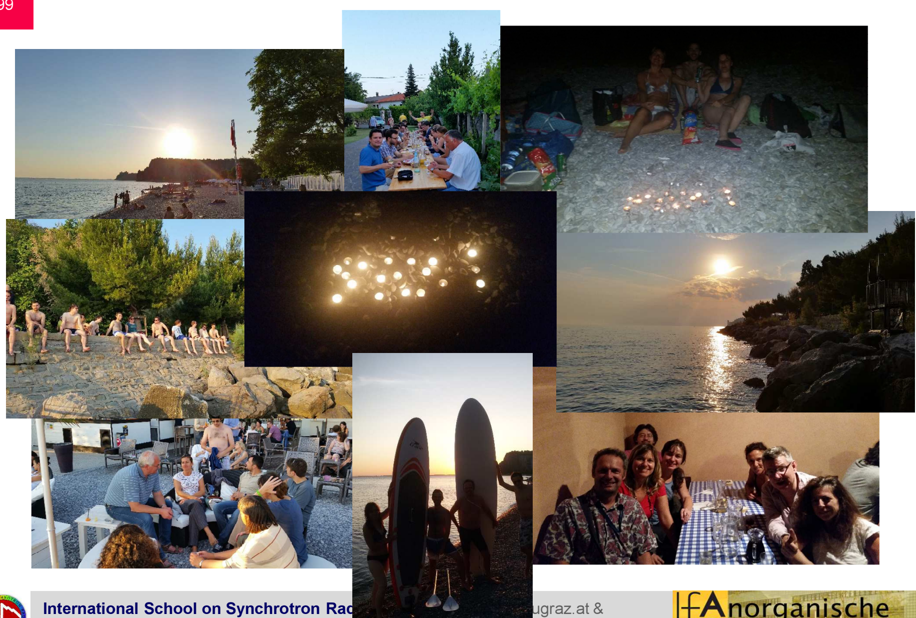

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