Karlsruhe Institute of Technology

Universität Bielefeld

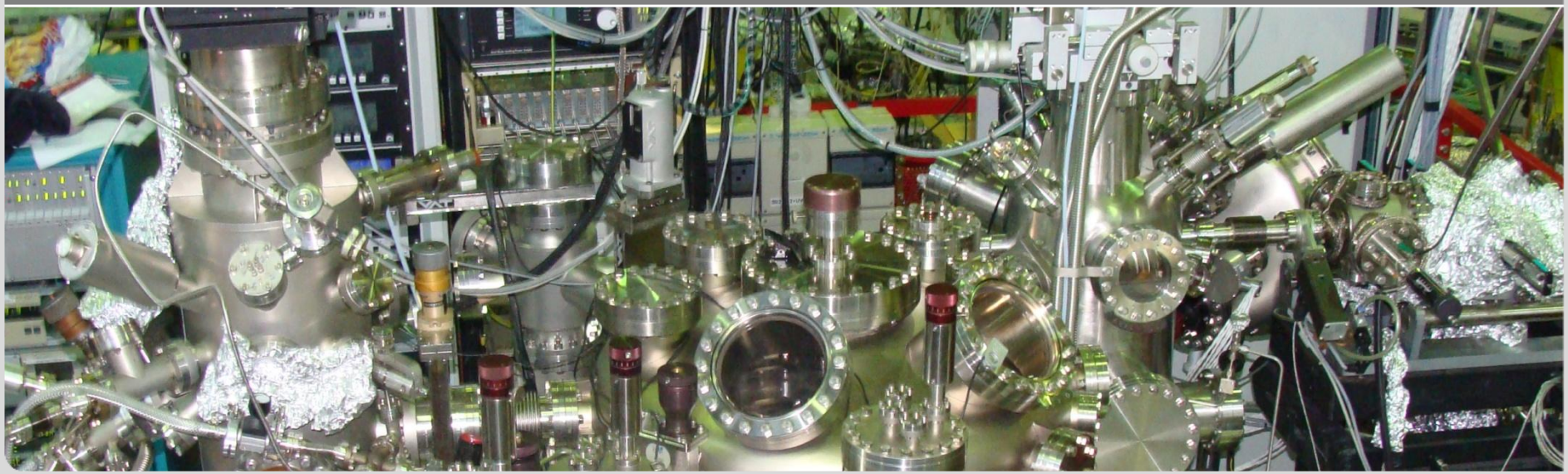
In situ UHV growth and XPS/NEXAFS characterization of aromatic self-assembled monolayers on gold substrates

A. Nefedov, M. Naboka, Ch. Wöll

Karlsruhe Institute of Technology

H.Muzik, A. Turchanin, A. Golzhäuser

University of Bielefeld

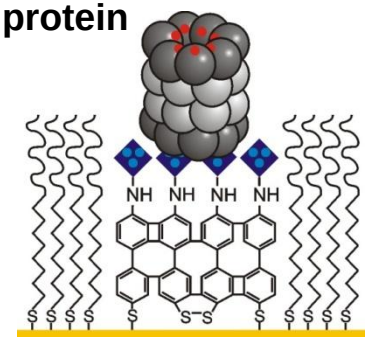


Motivation

Preparation

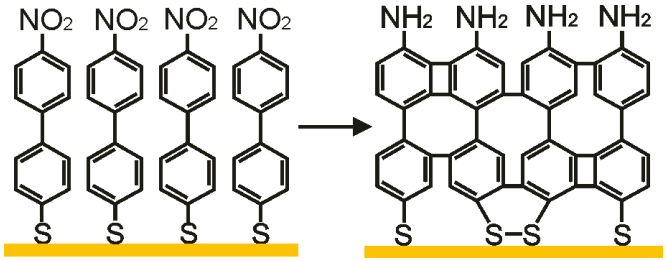
Modification ⟷ Functionalization

Functional immobilization of protein



A. Turchanin et al
Adv. Mater. 20 (2008) 471

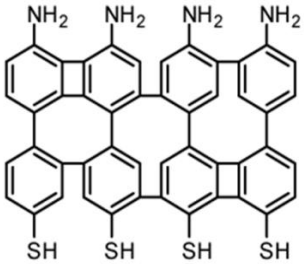
Electron induced generation of functional groups



A. Gölzhäuser et al, Adv. Mater. 13, 806 (2001)

A. Turchanin et al, Small 3, 2114 (2007)

Janus nanomembranes



A. Turchanin, AVS2011,
Talk Thursday (GR-NS-PS-SS-ThM4)

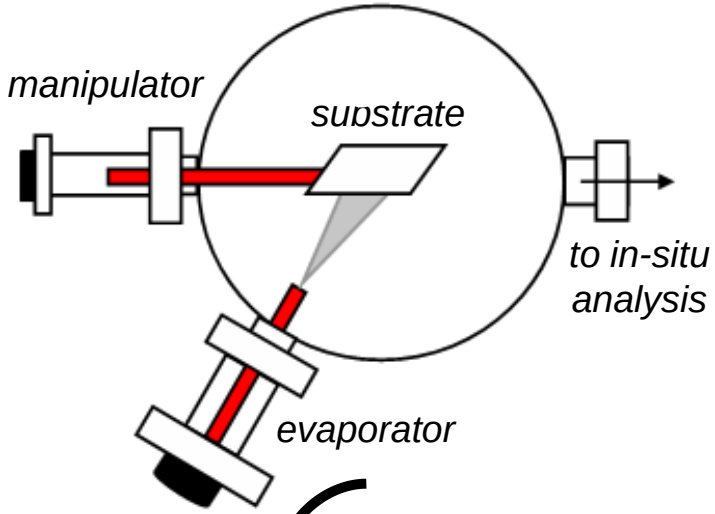
In situ characterization: XPS, NEXAFS

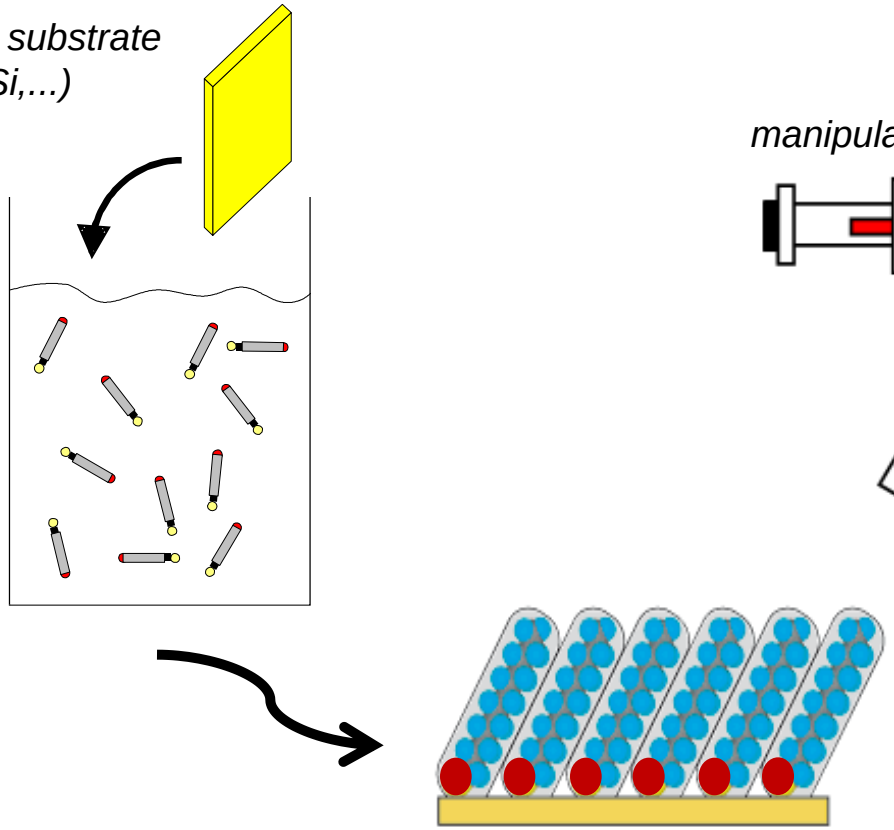
SAMs preparation

solution preparation

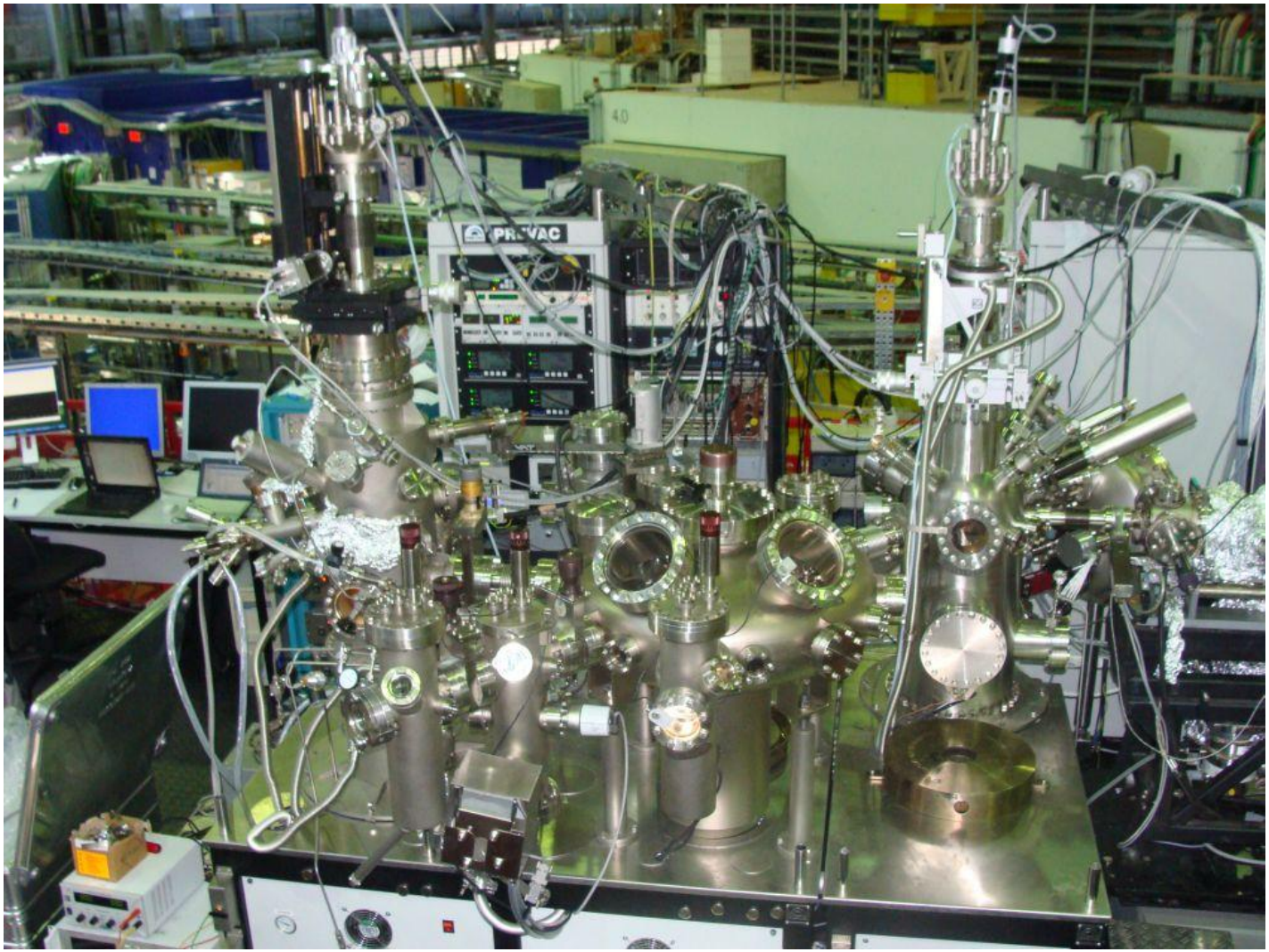
Immersion of a substrate (Au, Ag, Si,...)

vapour deposition in vacuum

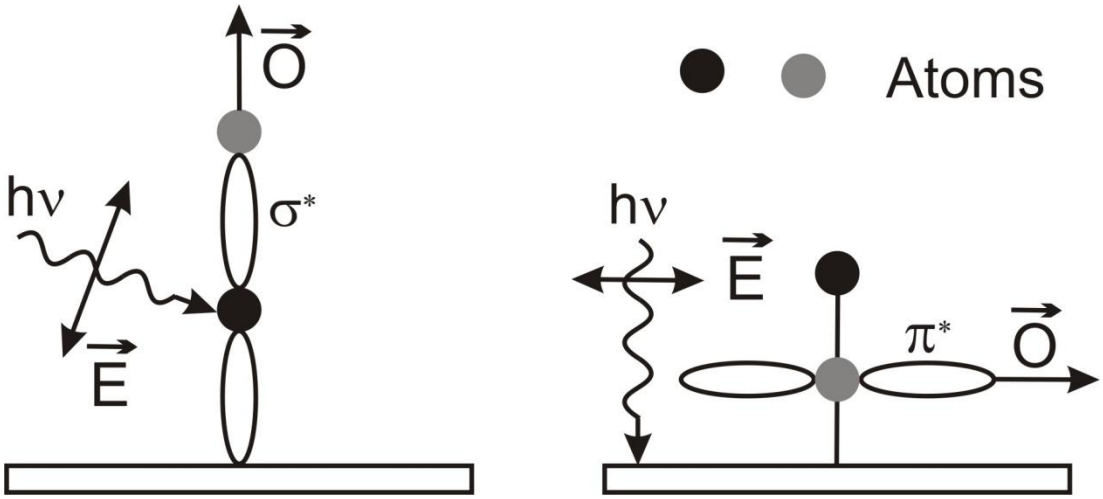




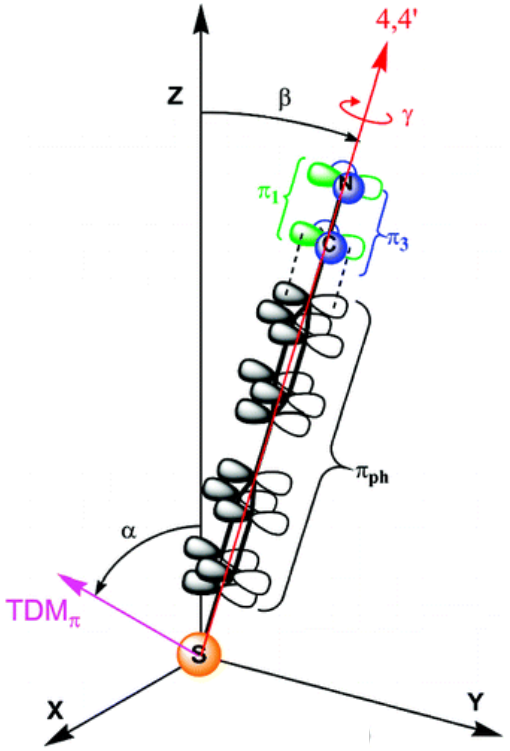
XPS/NEXAFS endstation @ BESSY II



NEXAFS Spectroscopy – tool for determination of SAMs molecule orientation



$$I(\alpha,\theta) = A\{P(1/3)[1 + (1/2)(3\cos^2\theta - 1)(3\cos^2\alpha - 1)] + (1 - P)(1/2)\sin^2\alpha\}$$



$\cos(\alpha) = \sin(\beta)\cos(\gamma)$

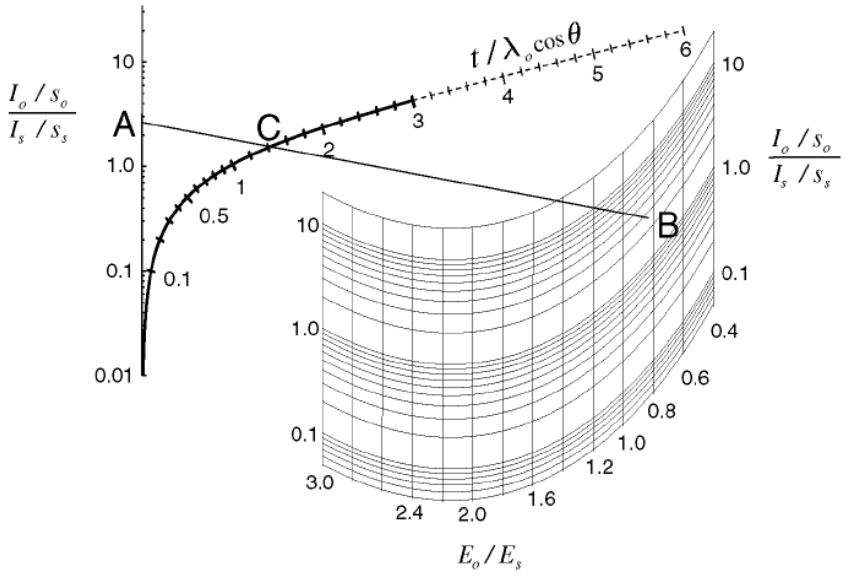
N. Ballav et al, JACS, 129, 15146, 2007

Coverage determination: thickogram

$$I_s/s_s = \exp(-t/\lambda_s \cos\theta)$$

$$I_o/s_o = 1 - \exp(-t/\lambda_o \cos\theta)$$

$$\ln\left(\frac{I_o/s_o}{I_s/s_s}\right) - \left[\left(\frac{E_o}{E_s}\right)^{0.75} - \frac{1}{2}\right]\frac{t}{\lambda_o \cos\theta} - \ln 2 = \ln\sinh\left(\frac{t}{2\lambda_o \cos\theta}\right)$$

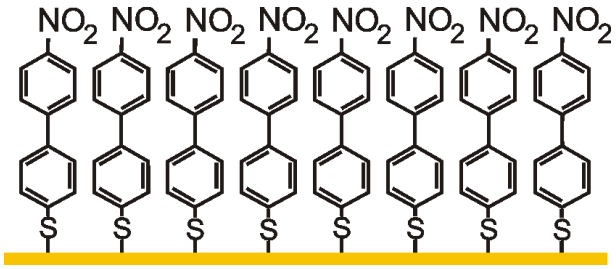


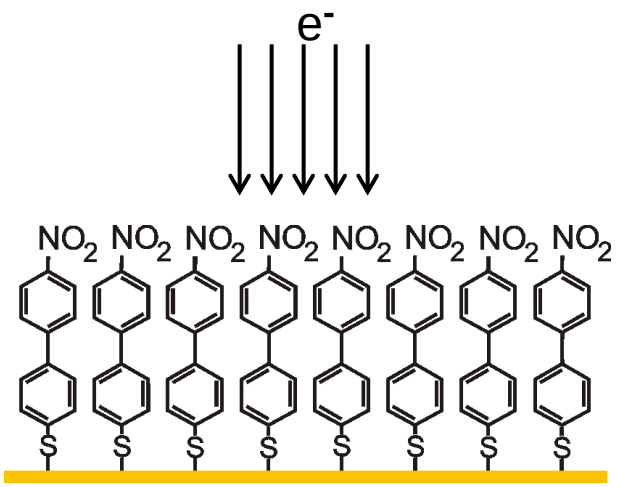
- I_s Intensity substrate
- I_O Intensity overlayer
- S_s Intensity infinite substrate
- S_O Intensity infinite overlayer
- E_s Kinetic energy
- E_O Kinetic energy
- λ_O Attenuation length of overlayer electrons

Peter J Cumpson *Surf. Interface Anal.* **29**, 403–406 (2000)

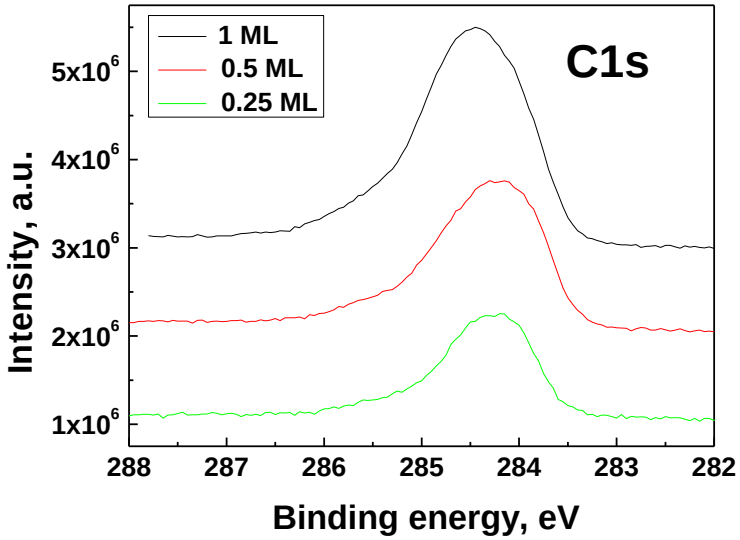
Layout of the experiment

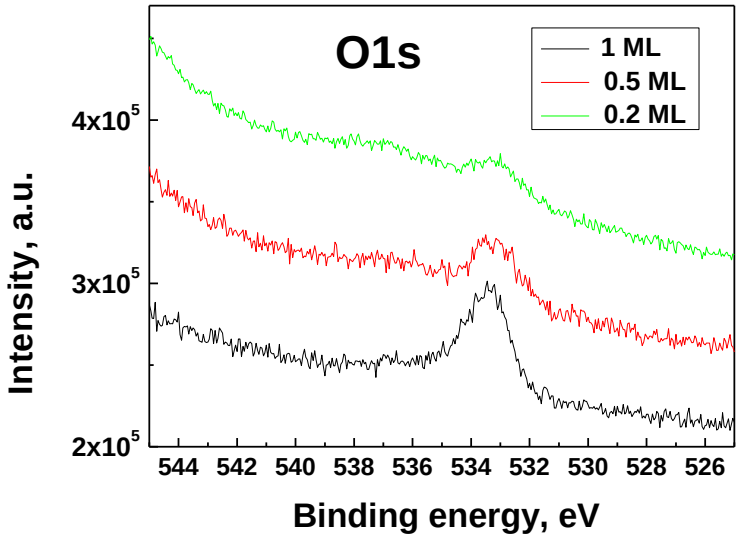
1. Deposition of NBPT fom Knudsen cell: T=80-100°C, t=1-30min, 1-4 steps , for some samples – additional annealing (T=100°C, t=10 min-10h)
2. Characterisation
   XPS: C1s, N1s, O1s, S2p, Au4f
   NEXAFS: C-, N- and O-K edges
3. Irradiation with electrons, E=100 eV, I= 0.5mA, stepwise, t=20 s - 5 min, t_{tot}=20 min, 45 mC/cm^2
4. Characterisation

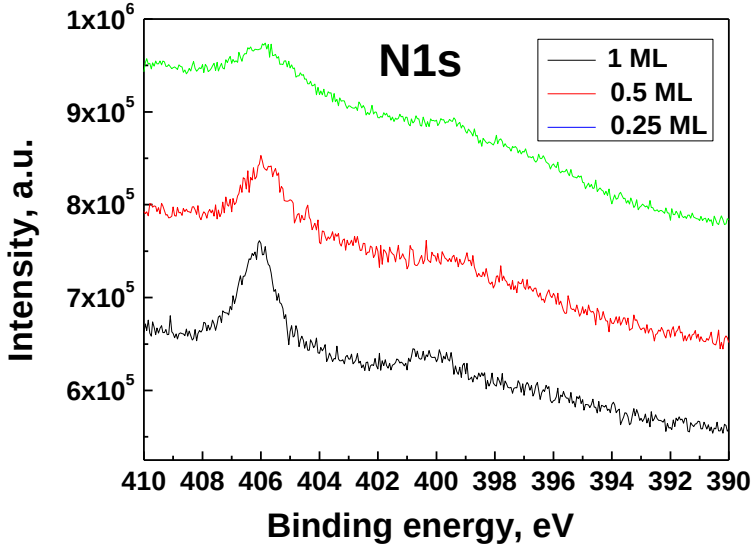




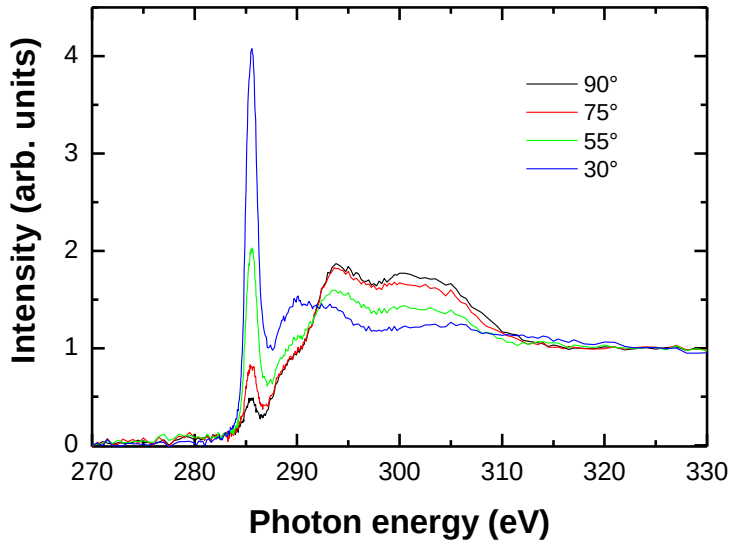
XPS results

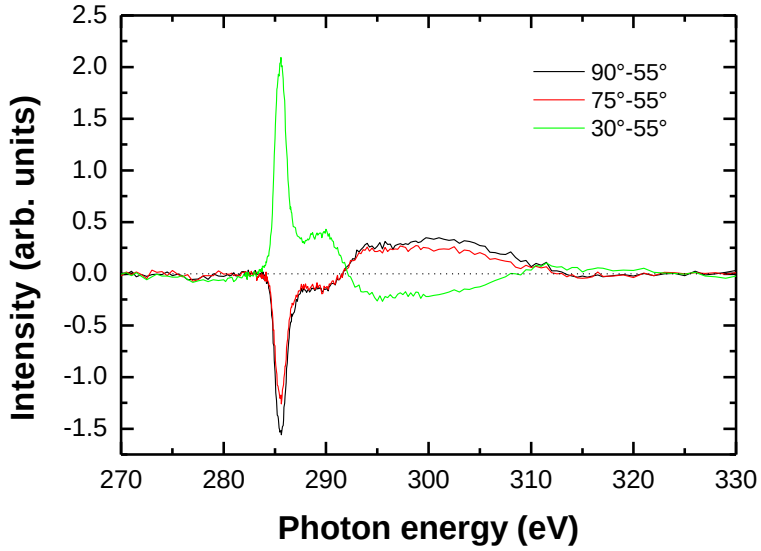

C1s
1 ML
0.5 ML
0.25 ML
Intensity, a.u.
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
288
287
286
285
284
283
282
Binding energy, eV

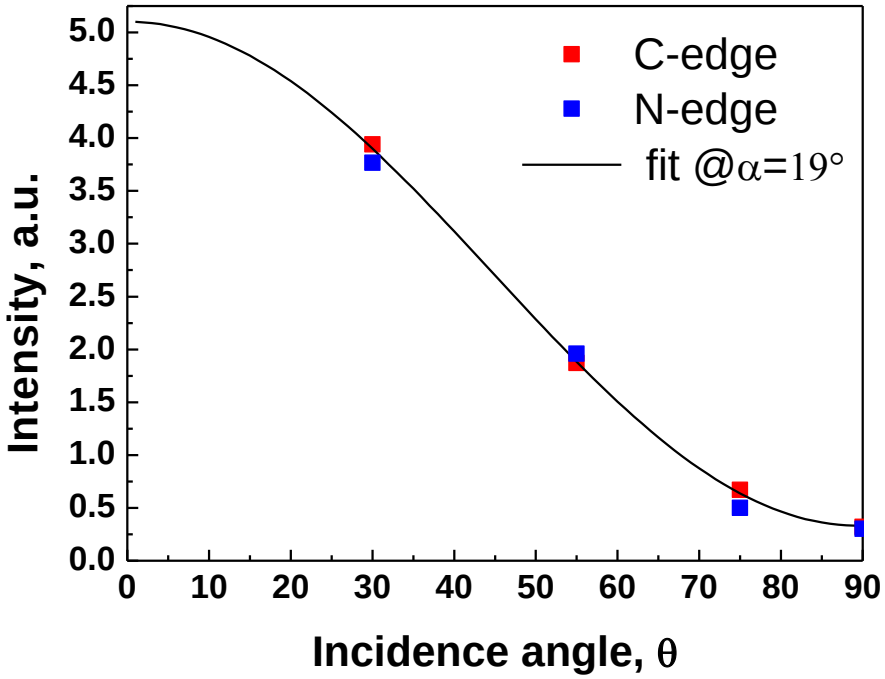

O1s
1 ML
0.5 ML
0.2 ML
Intensity, a.u.
4x10^5
3x10^5
2x10^5
544
542
540
538
536
534
532
530
528
526
Binding energy, eV


N1s
1 ML
0.5 ML
0.25 ML
Intensity, a.u.
1x10^6
9x10^5
8x10^5
7x10^5
6x10^5
410
408
406
404
402
400
398
396
394
392
390
Binding energy, eV

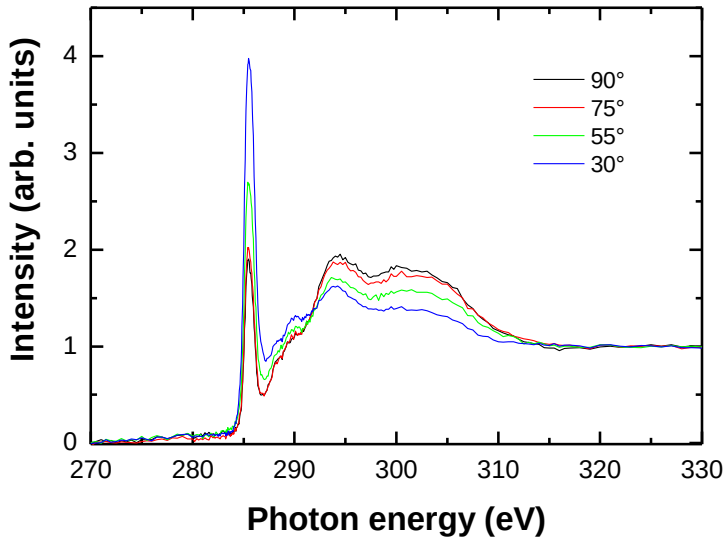
C-edge NEXAFS: 0.25ML NBPT/Au

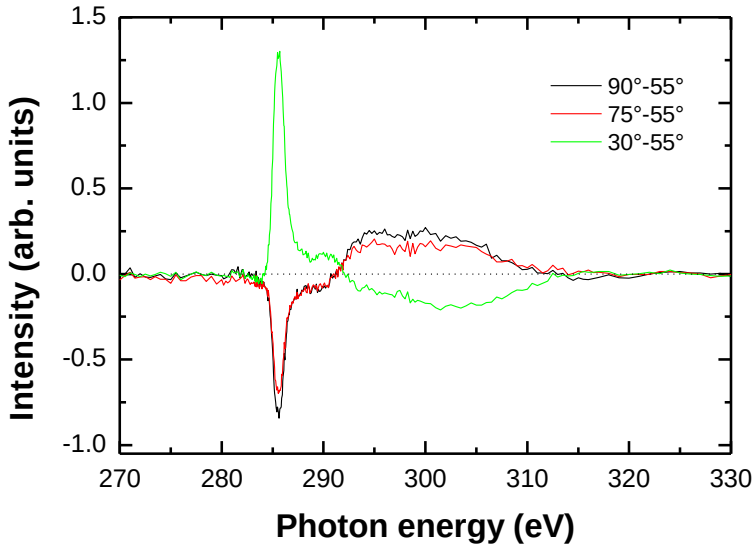


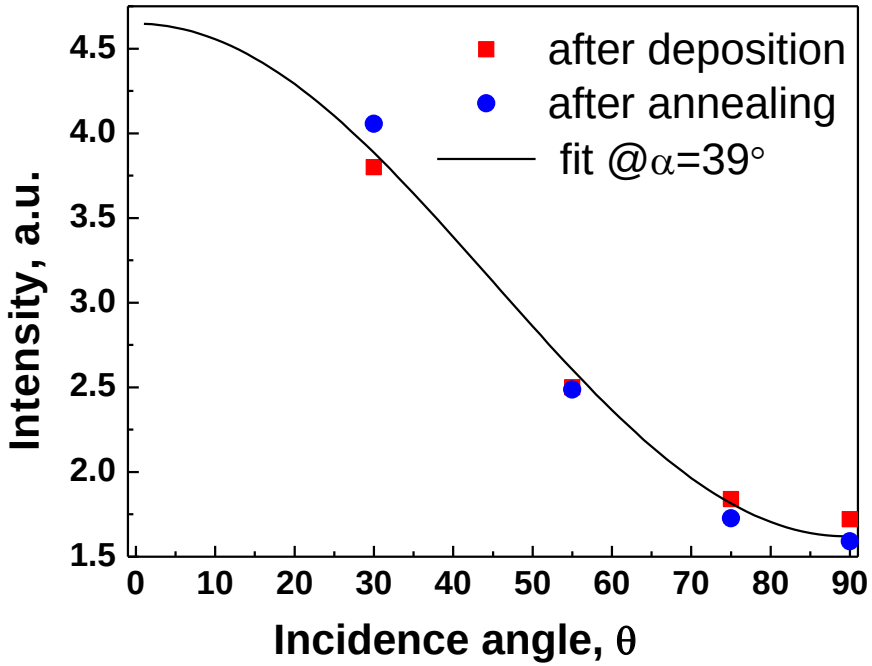




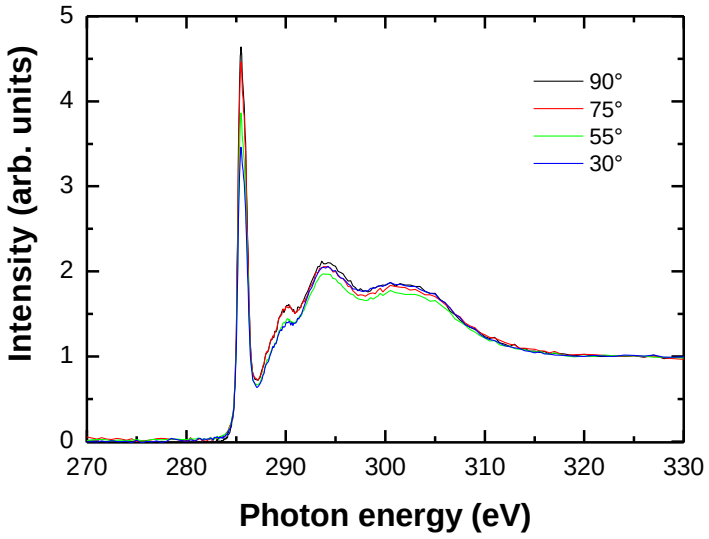
C-edge NEXAFS: 0.5ML NBPT/Au

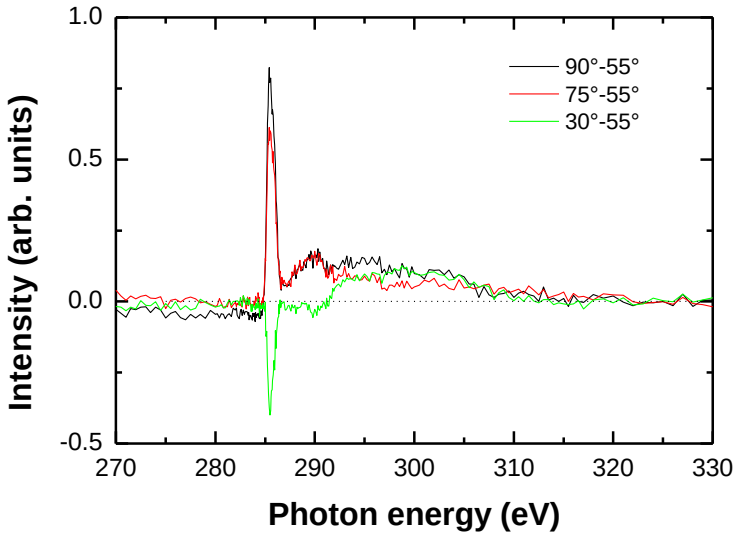


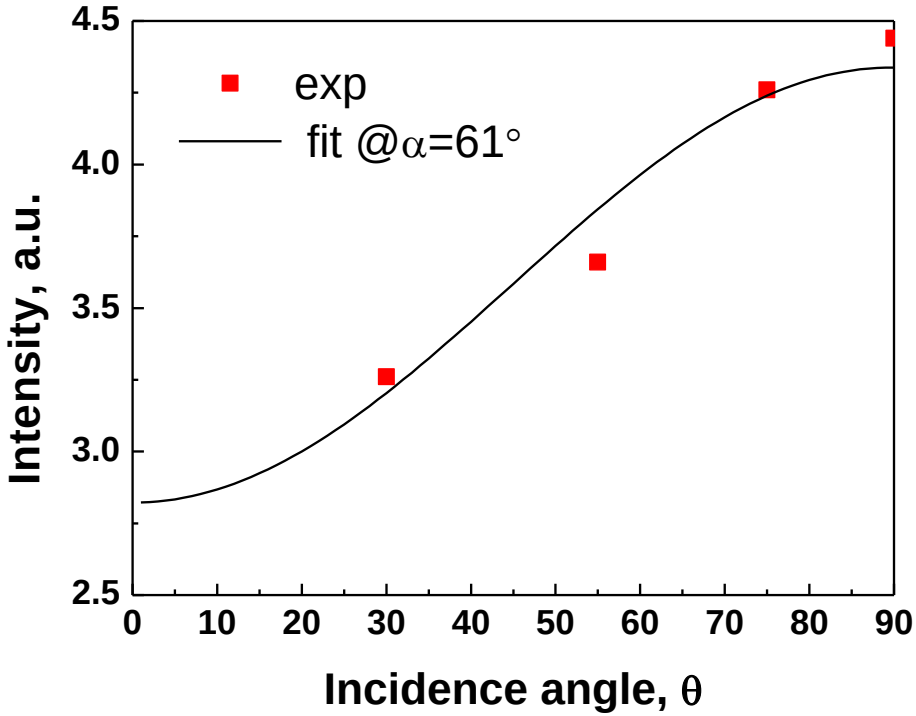




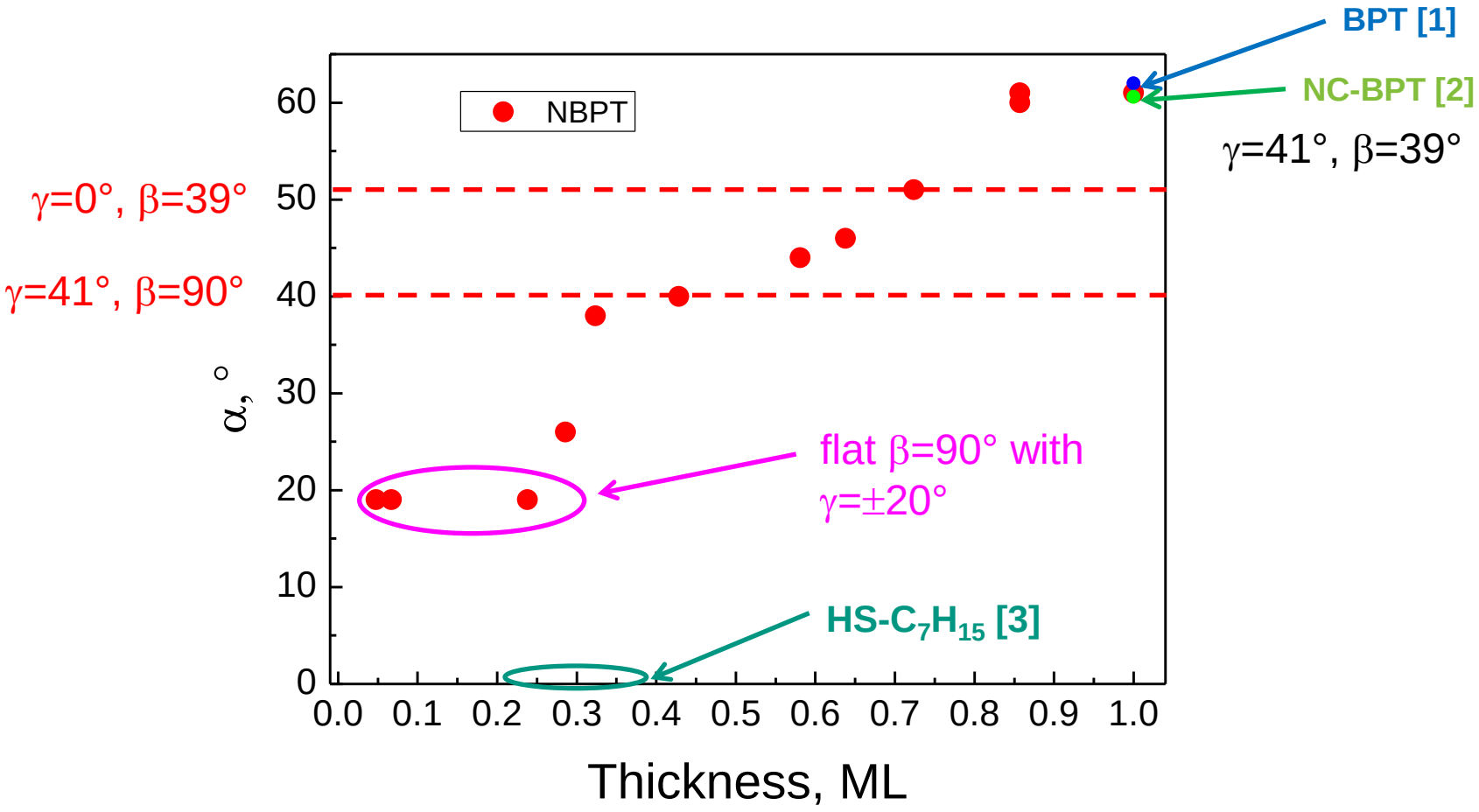
C-edge NEXAFS: 1ML NBPT/Au







Coverage dependence of TDM angle

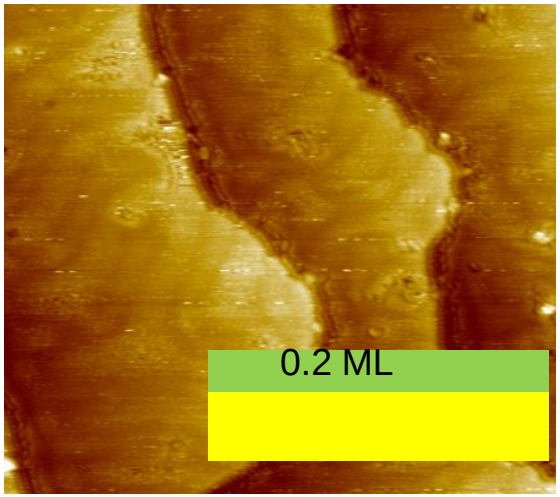


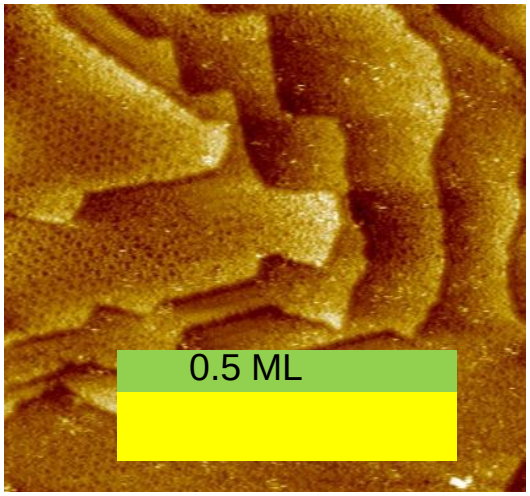
1. A. Turchanin et al, Langmuir, 25, 7342, 2009

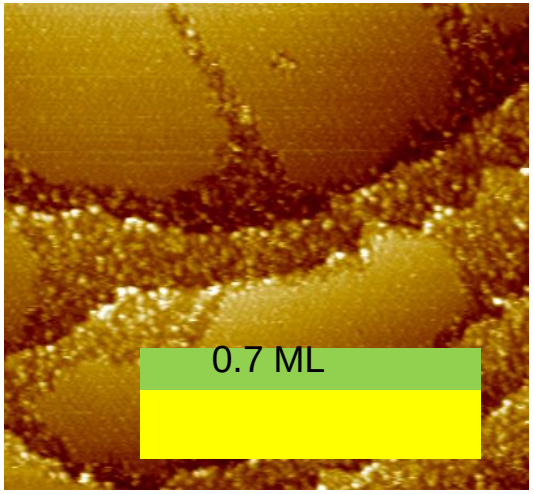
2. N. Ballav et al, JACS, 129, 15146, 2007

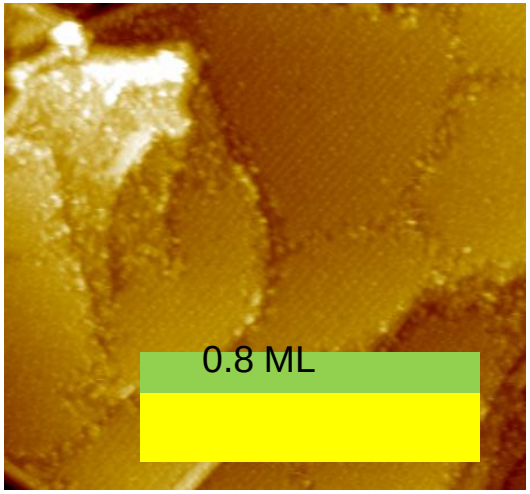
3. H.-J. Himmel et al, Langmuir, 13, 602, 1996

STM study of NBPT on Au(111): from sub-monolayers to 1ML



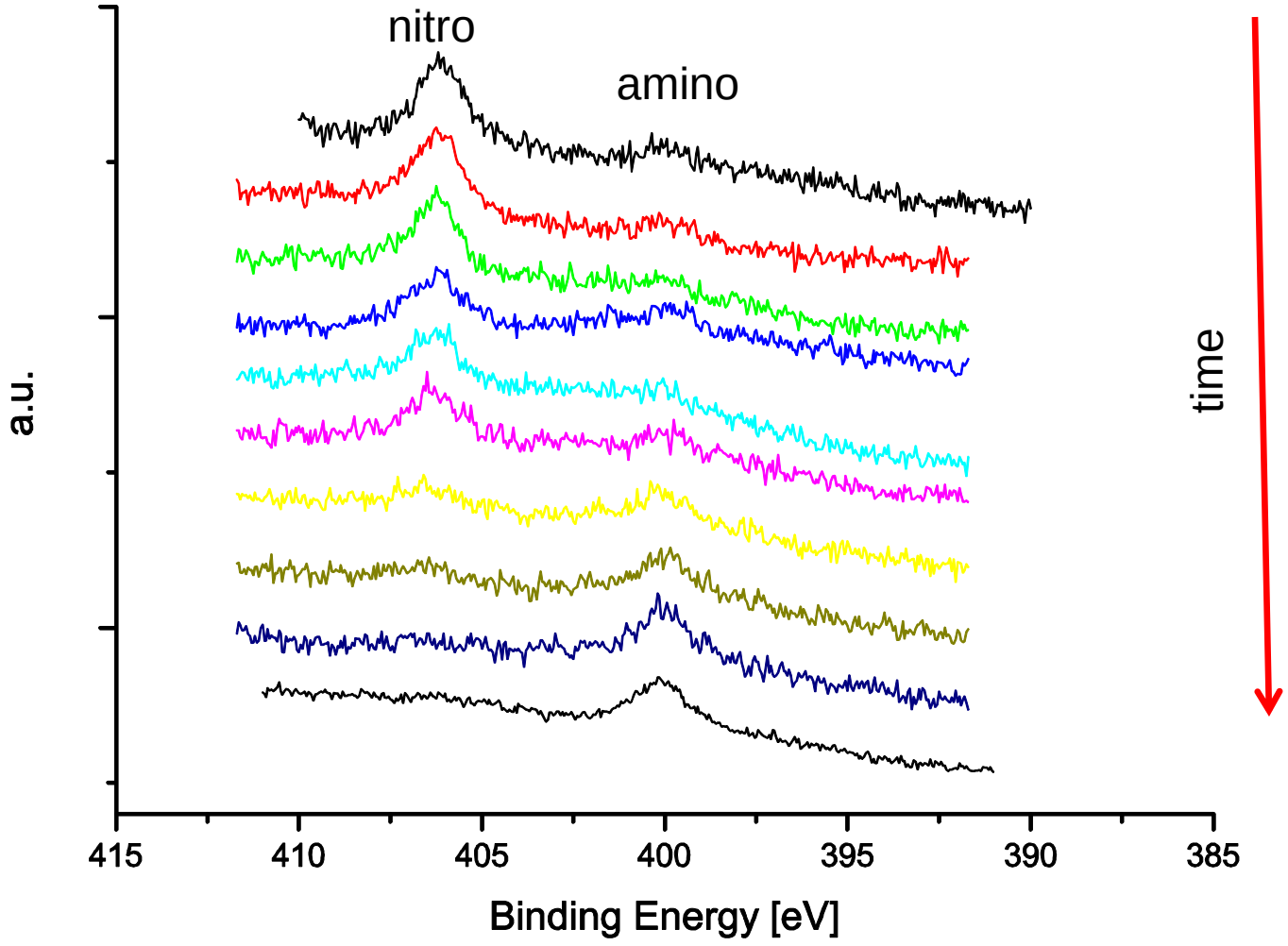




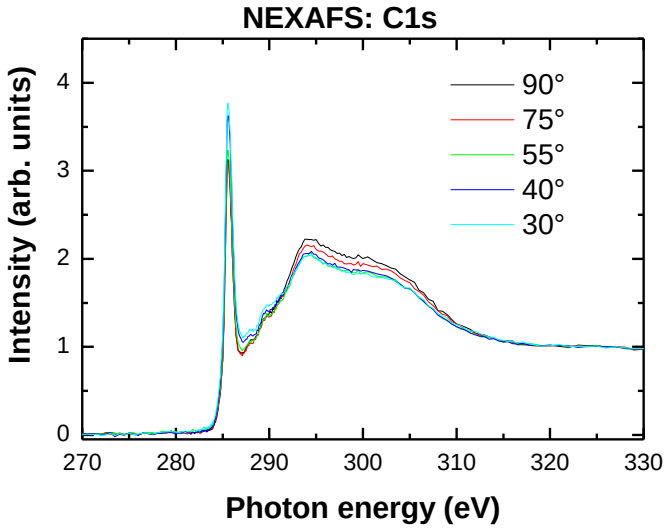


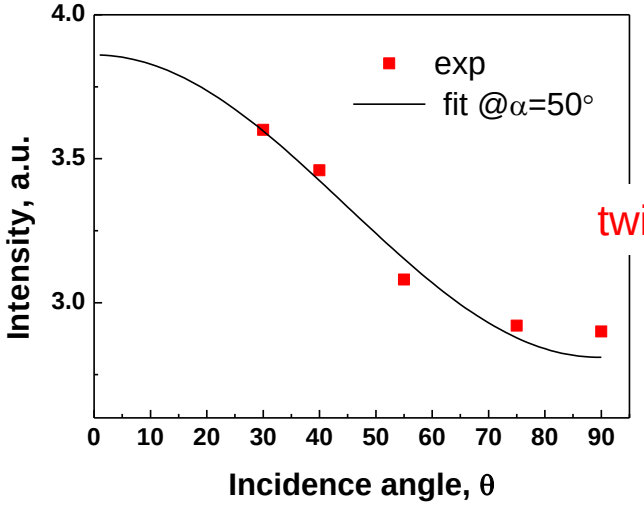
H. Muzik, A. Turchanin, A. Golhäuser , AVS2010

Irradiation: transition from nitro- to amino- functional groups

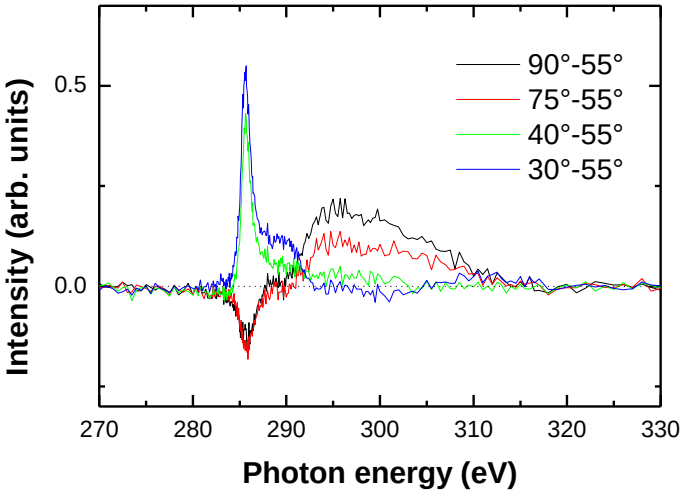


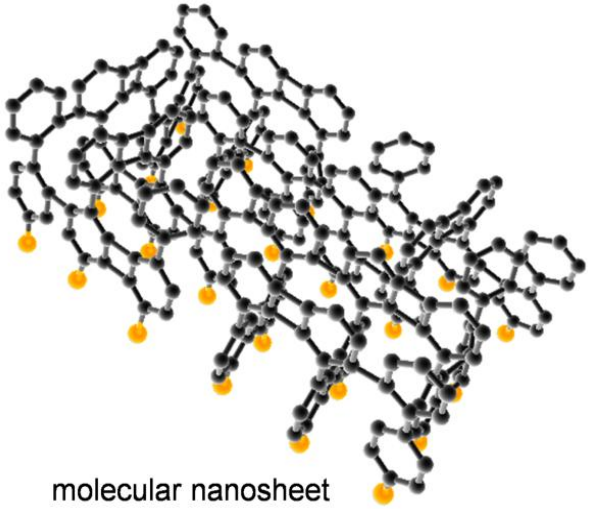
1ML NBPT/Au after e-irradiation



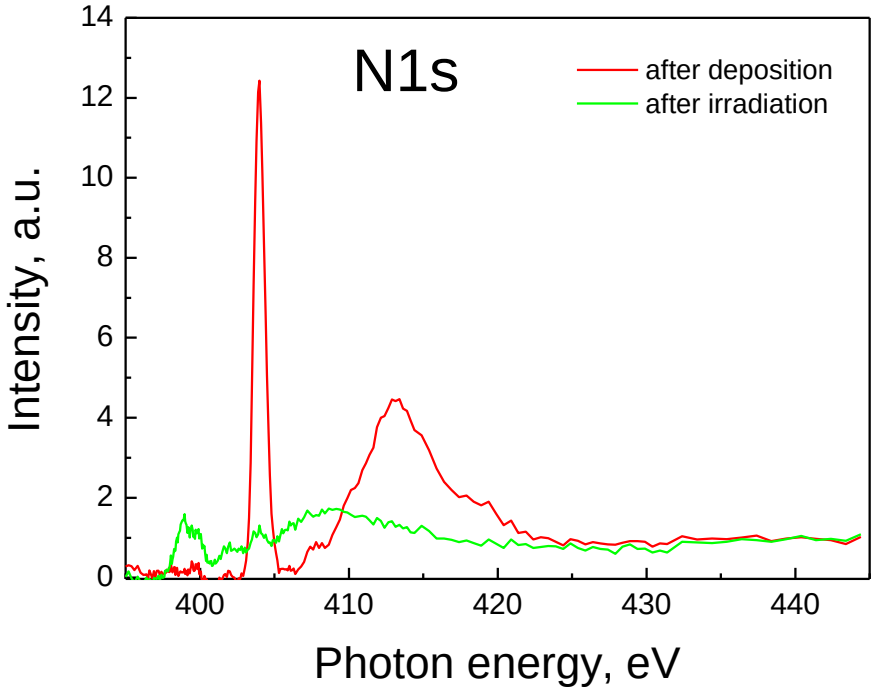


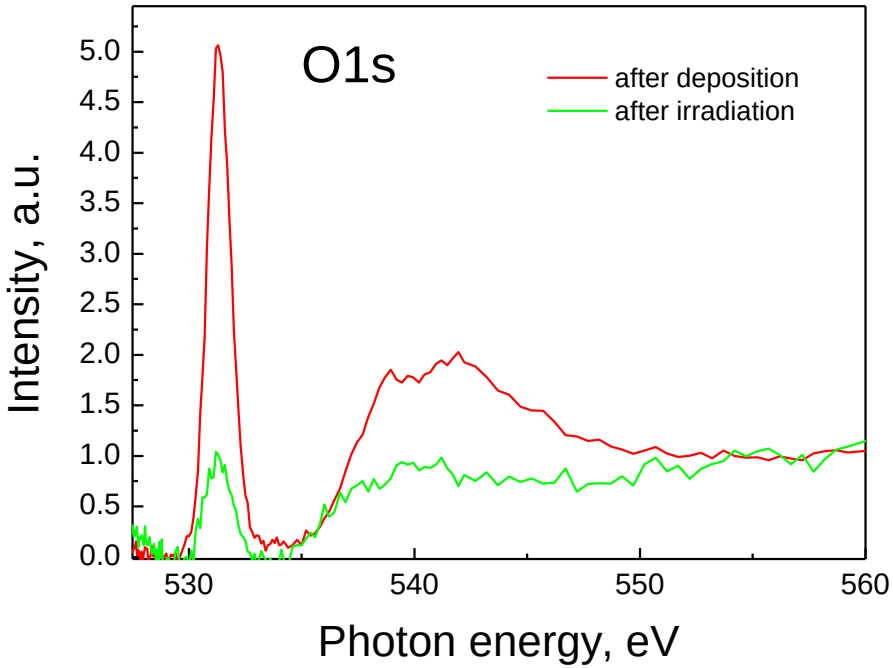
twist angle γ=0



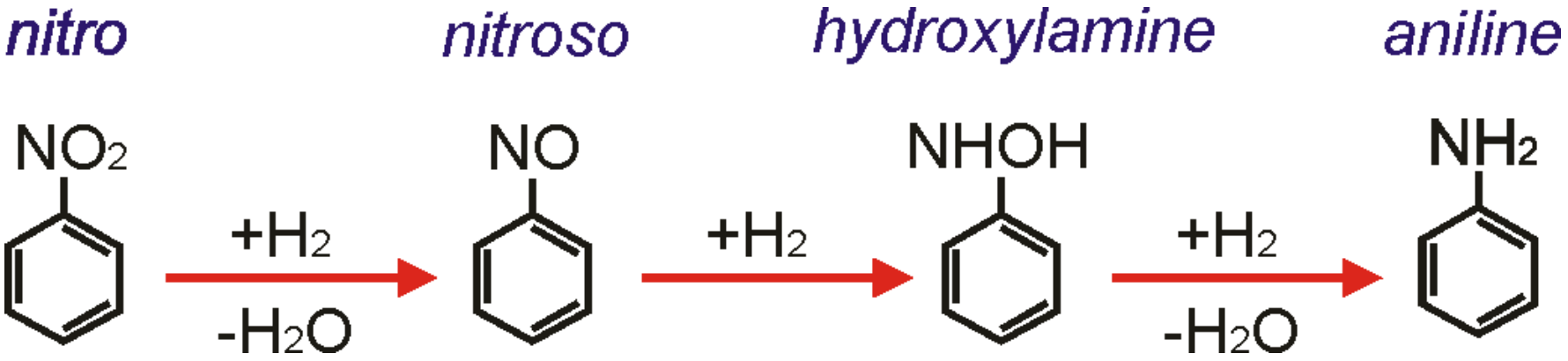

molecular nanosheet

Irradiadion: N- and O-edge NEXAFS results





Electron induced generation of functional groups: possible mechanism



F. Haber, Z. Elektrochem. 22, 506 (1898)
H.U. Blaser, Science 313, 312 (2006)

Summary

- At low coverages NBPT molecules are (almost) parallel to Au substrate, at coverage increase they start firstly to twist keeping the main molecular axis parallel to the surface. When the twist angle γ becomes about 40°, NBPT molecules stand up in up-right position forming self-assembled monolayer.
- After e-irradiation twist angle γ becomes 0°, resulting from cross-linking of phenyl rings, but keeping the same tilt angle β=39°.
- At transition from nitro to amino functional groups intermediate functional groups (nitroso, hydroxylamine) are also present.