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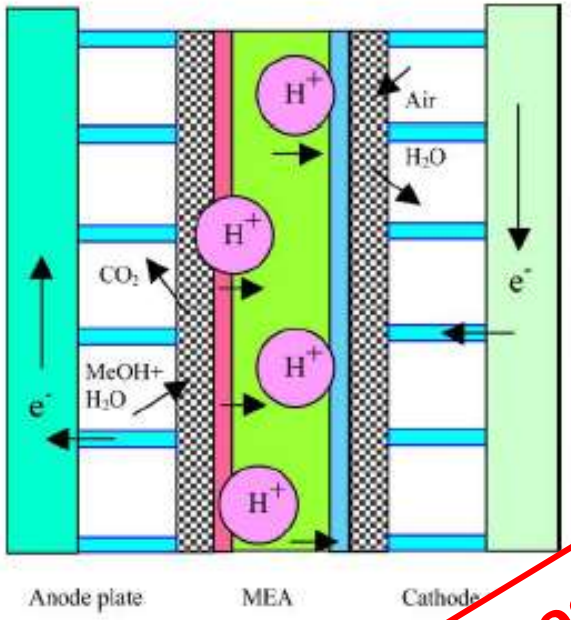
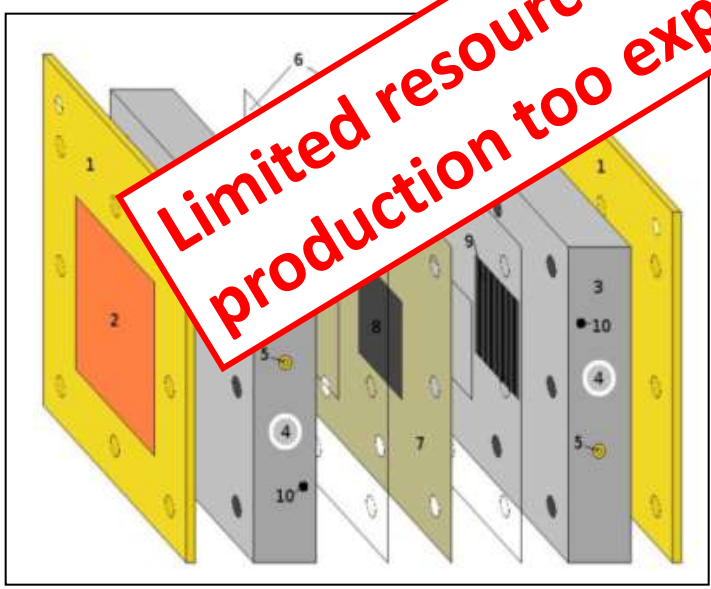
HAXPES investigation of nanostructured proton exchange membrane fuel cell catalysts

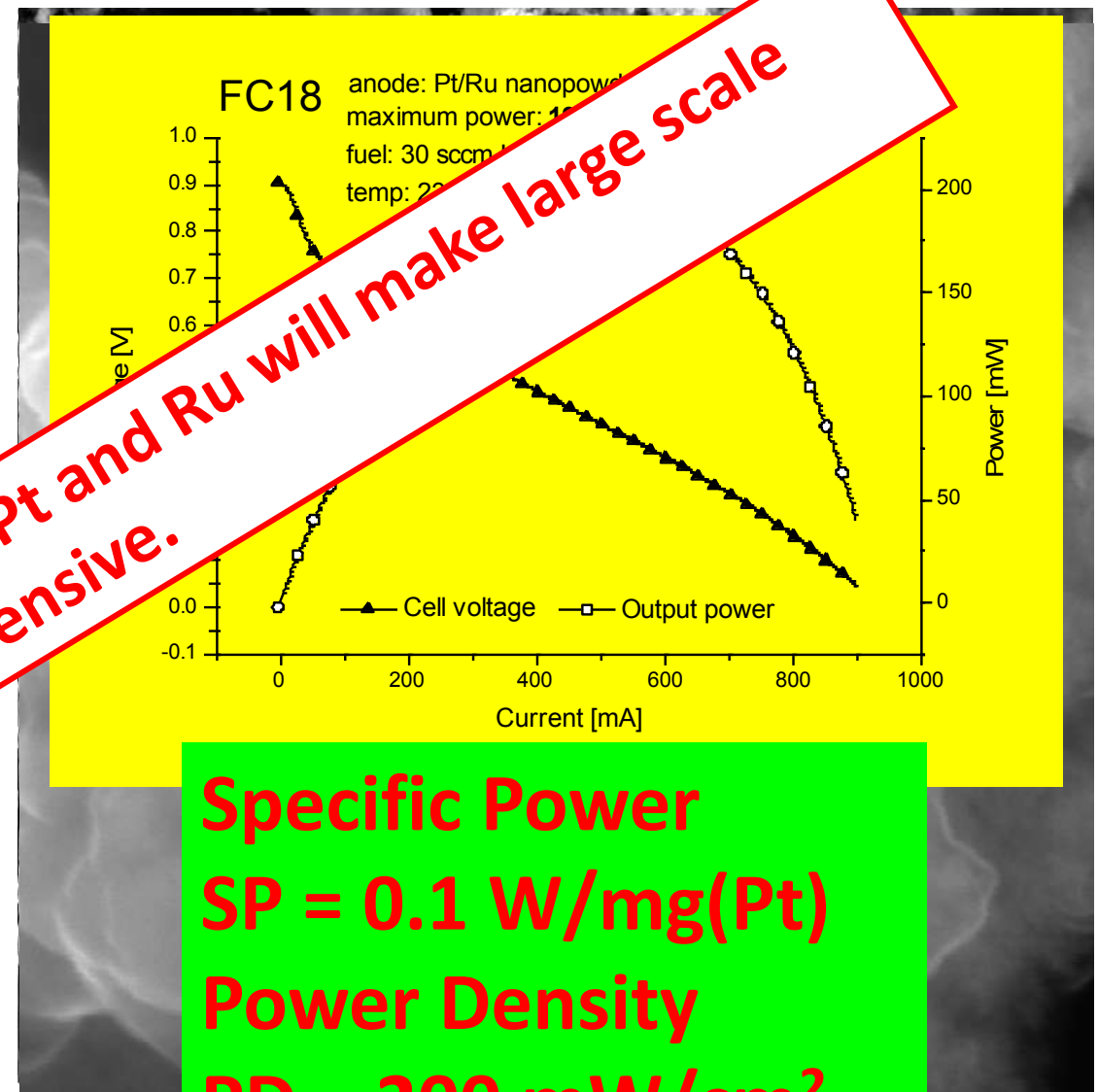
V. Matolín, I. Matolínová, H. Yoshikawa, K. Kobayashi, B. Detlefs

Charles University in Prague, Czech Republic
BL15XU, Spring-8, Japan
ID 32, ESRF, France

Polymer membrane fuel cell: Pt-Ru anode



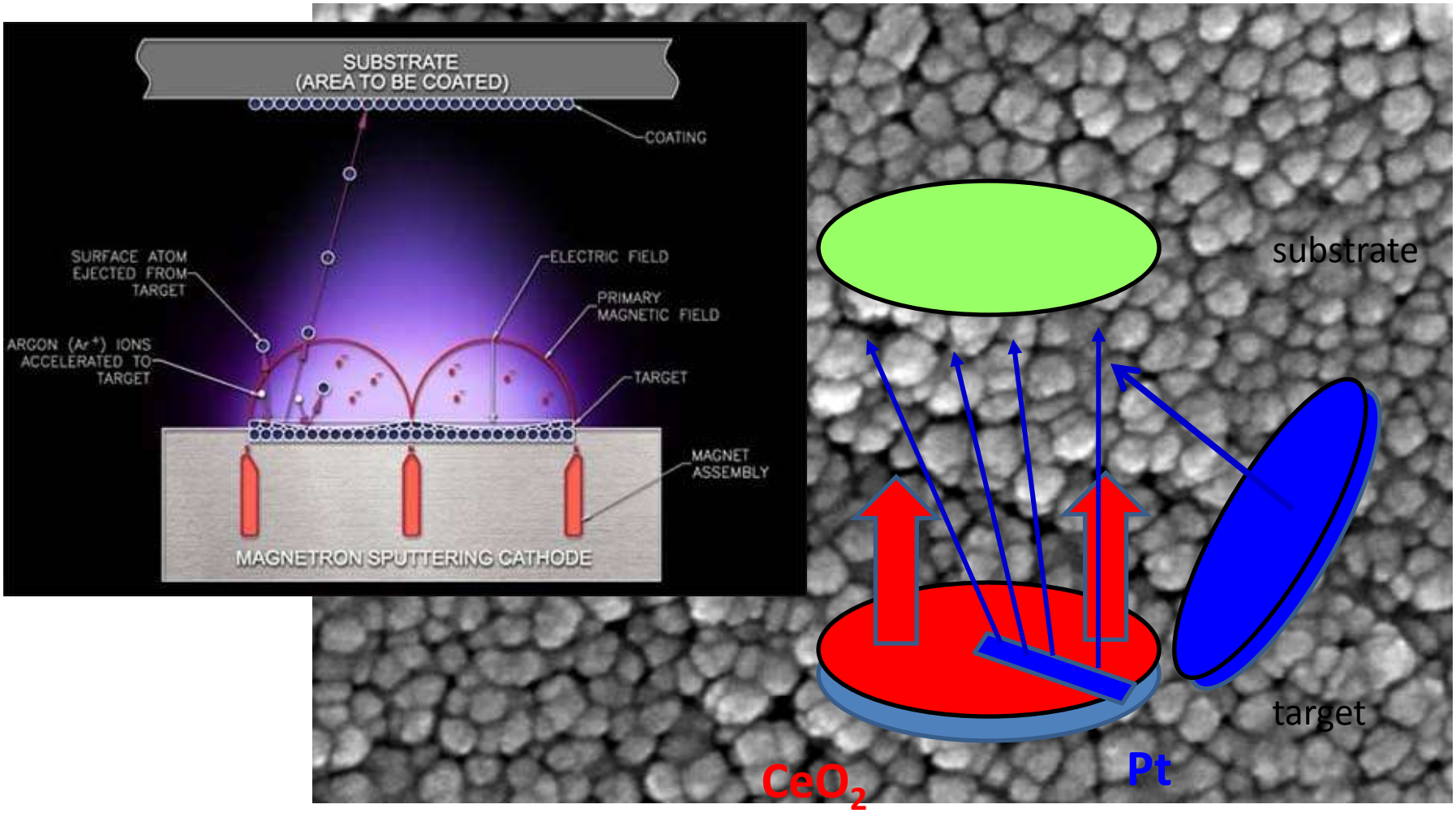




Limited resources of Pt and Ru will make large scale production too expensive.

Specific Power
SP = 0.1 W/mg(Pt)
Power Density
PD = 200 mW/cm^2

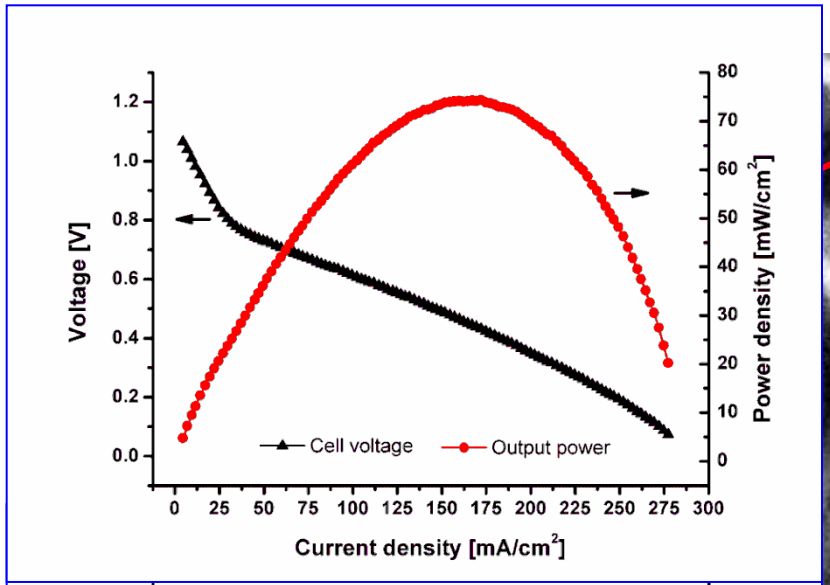
Preparation of Pt-CeO_2 catalyst by rf co-sputtering

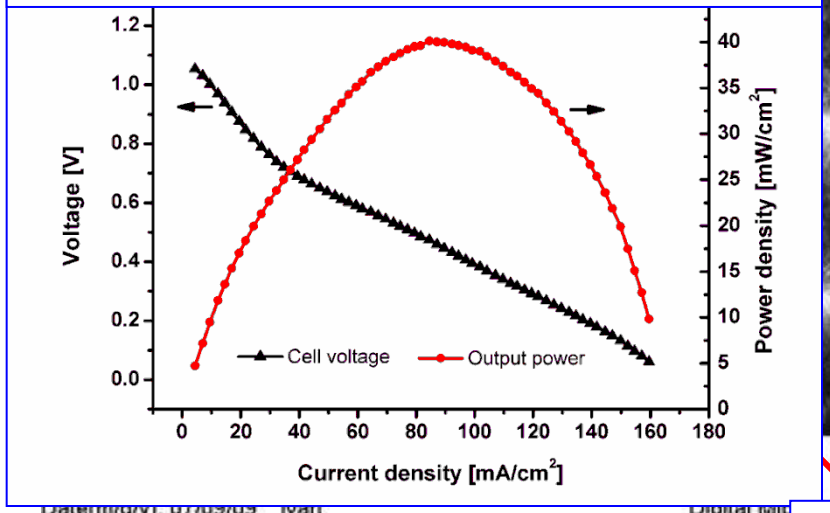


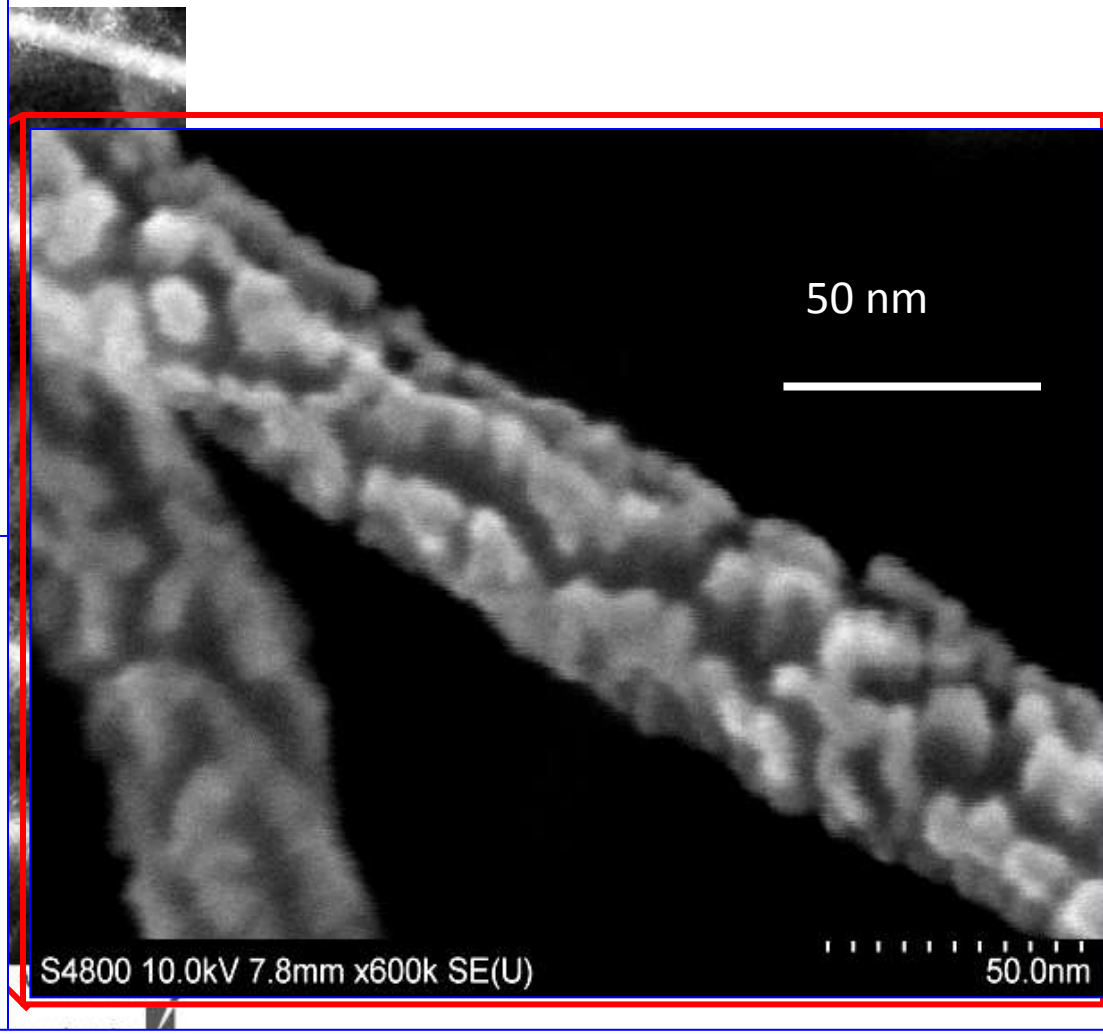
Pt-CeOx interaction: New catalytic properties

G. Vayssilov, …V. M. et al., **Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles, Nature Materials**, **10** (2011) 310

Pt-ceria/CNTs on GDL







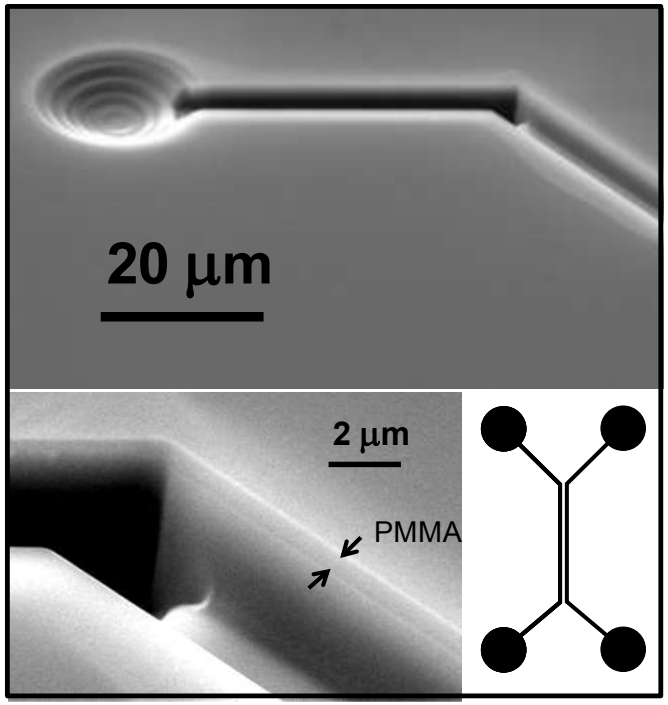
PD = 40 – 80 mW

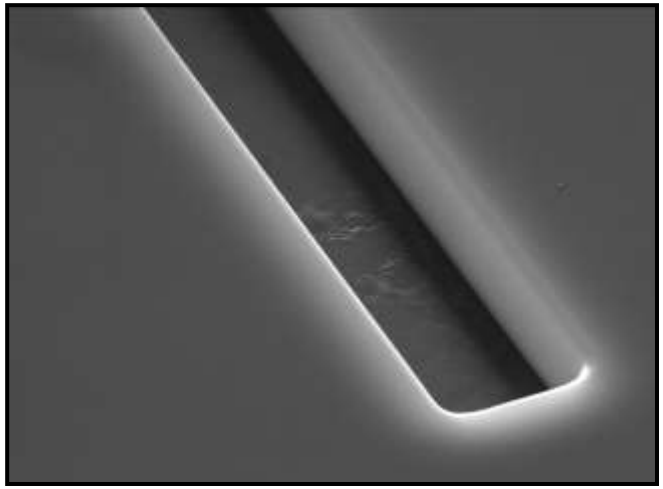
SP = 40 – 80 W/mgPt

R. Fiala,.., V.M. J Nanosci. Nanotechnol. 11 (2011) 5065

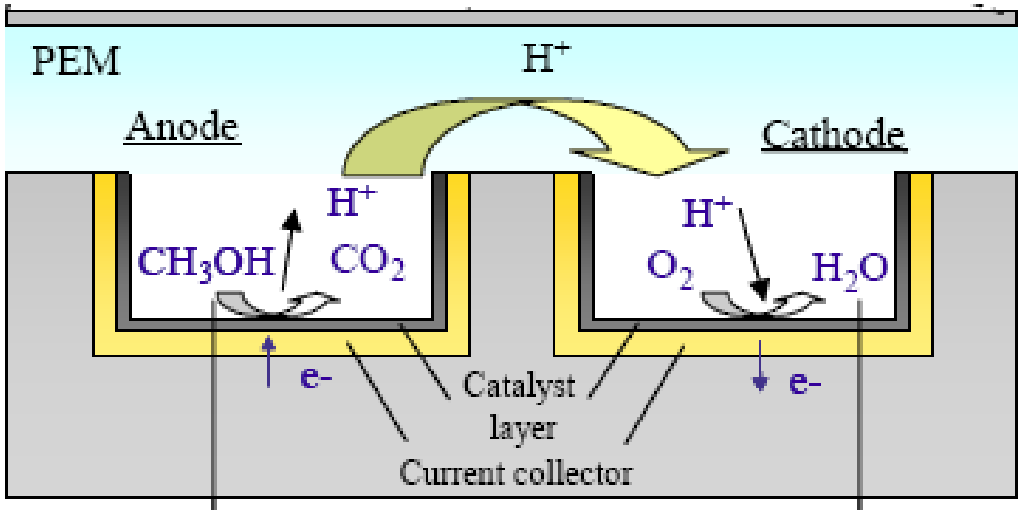
V.M. et al. Langmuir 26 (2010) 12824

Planar μ-PEMFCs, powering of integrated circuits



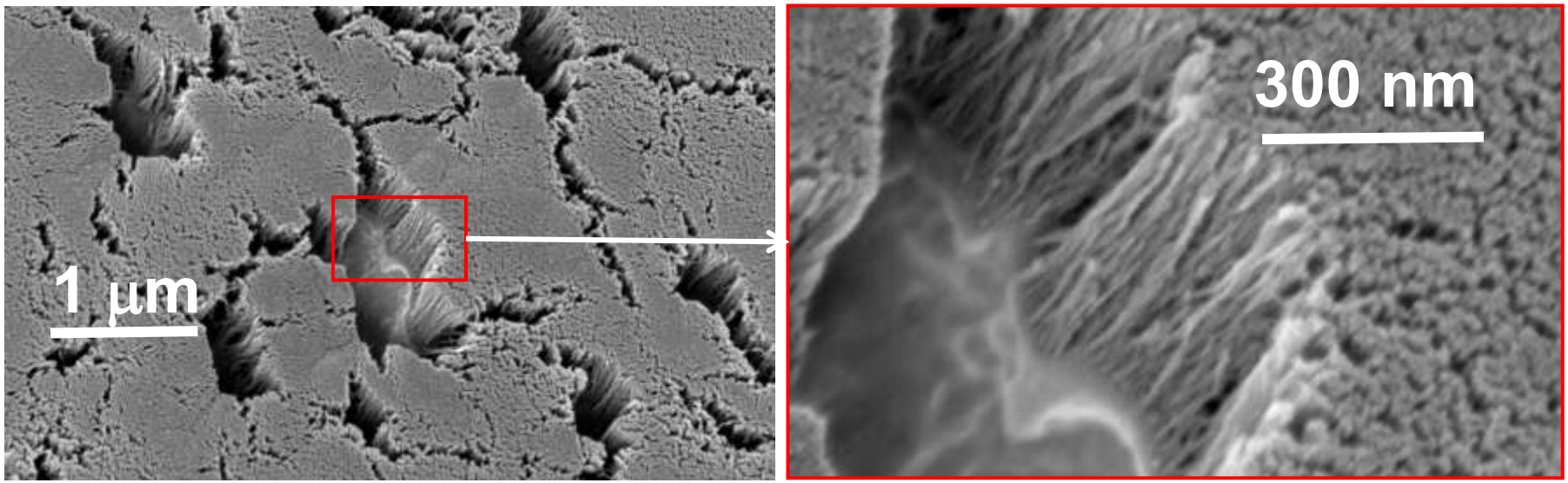


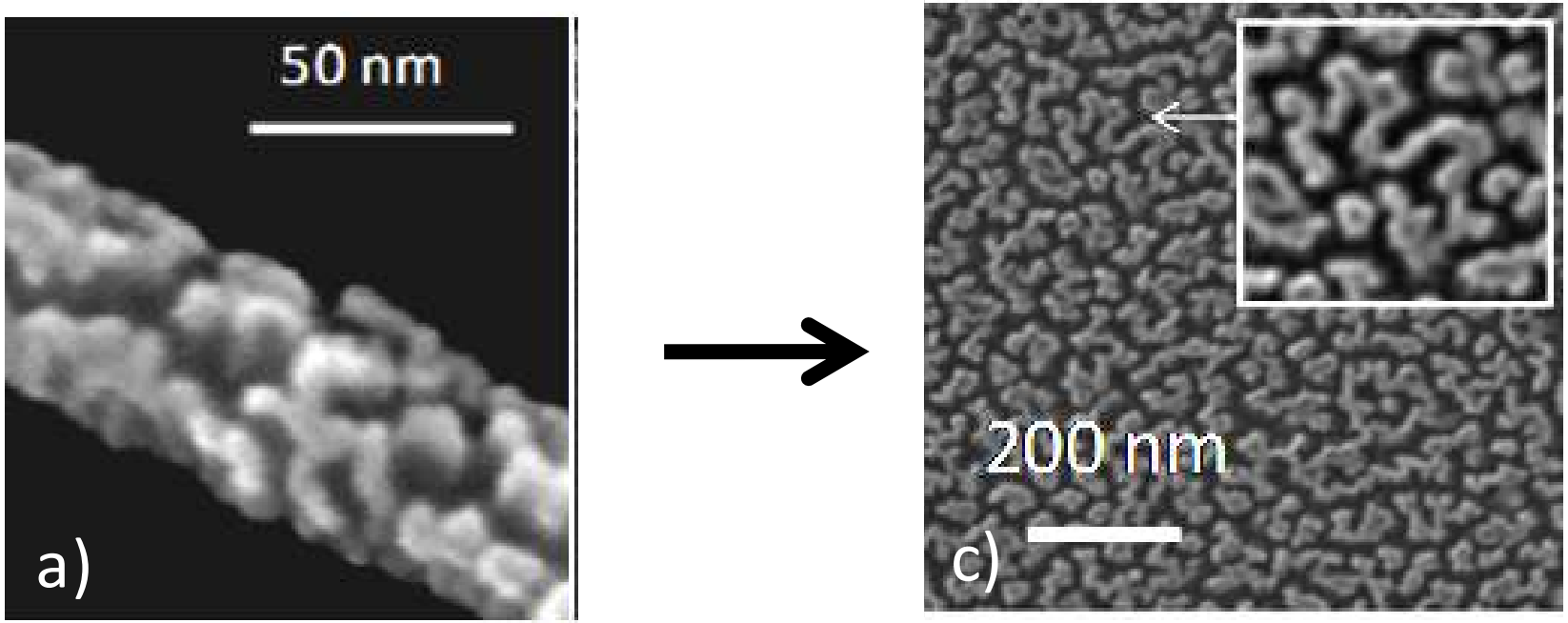
Focus Ion Beam (FIB) milling, Ion Beam Lithography, Catalyst deposition by PVD



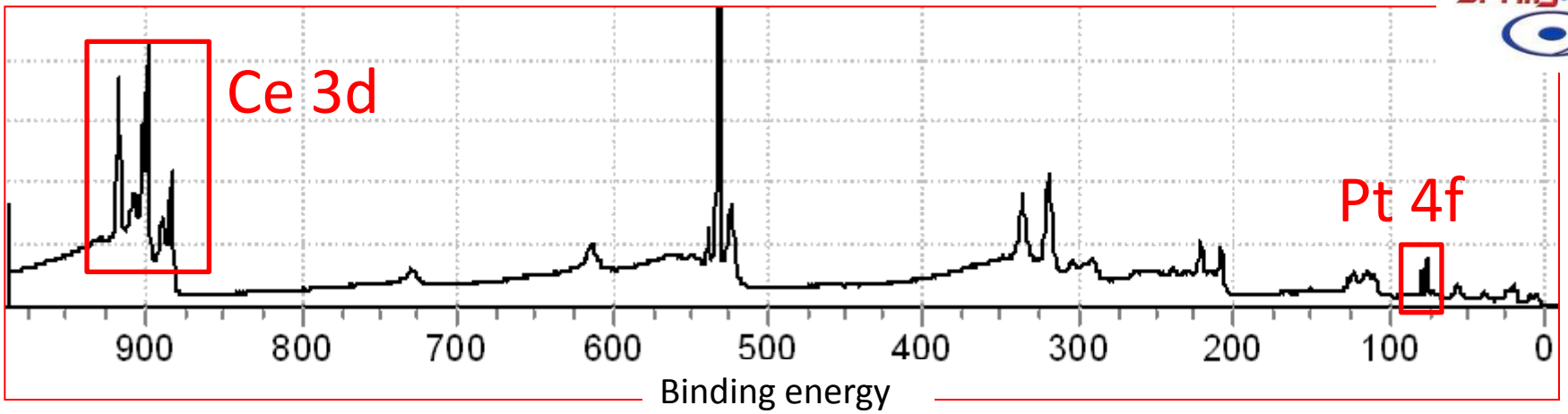
Methanol, hydrogen

Air

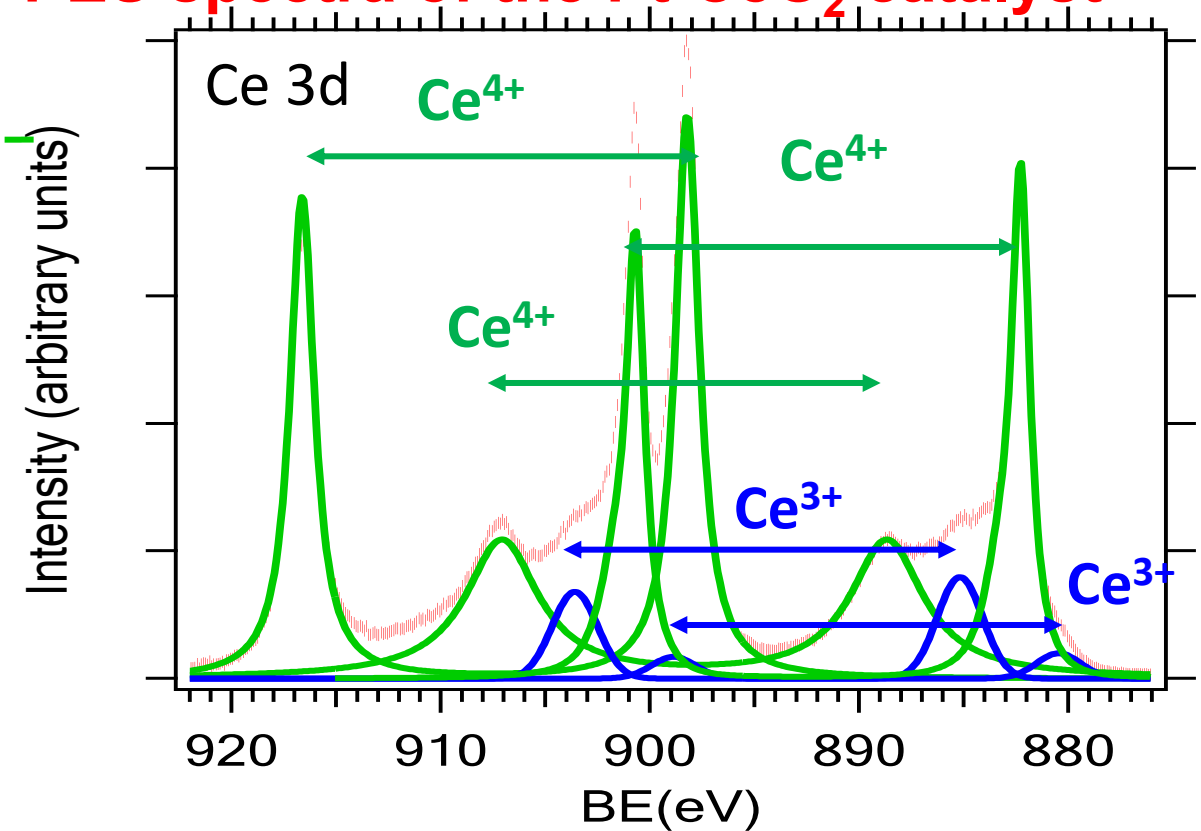


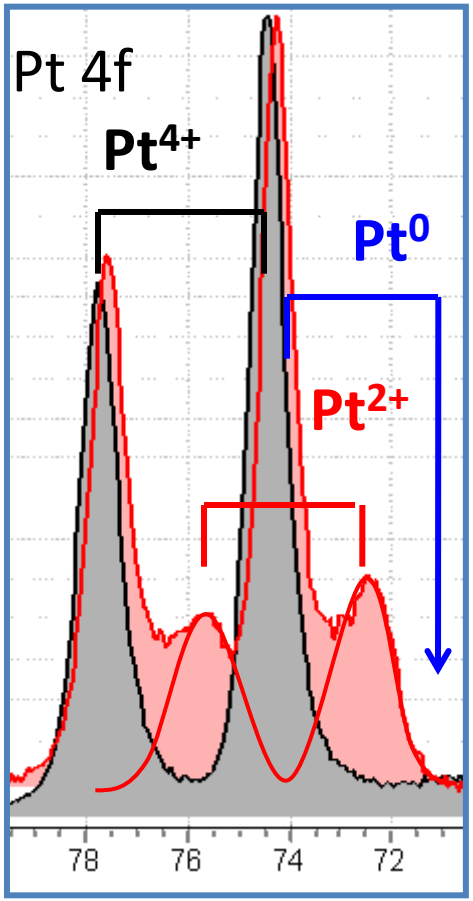


Carbon foil substrate

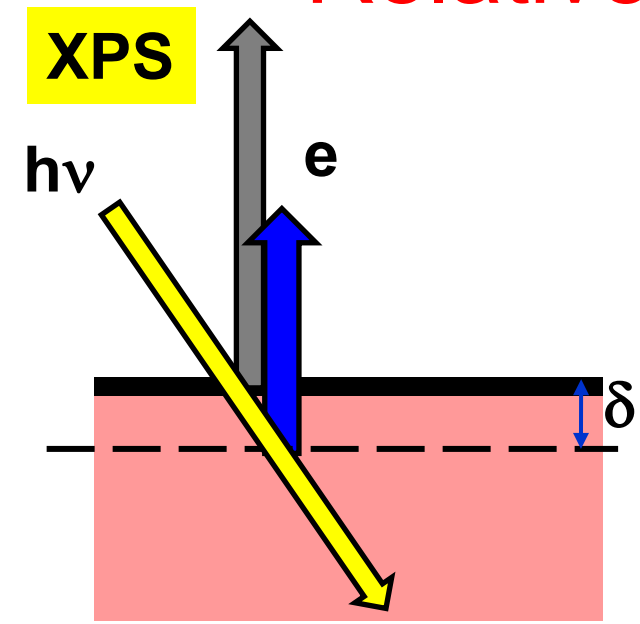


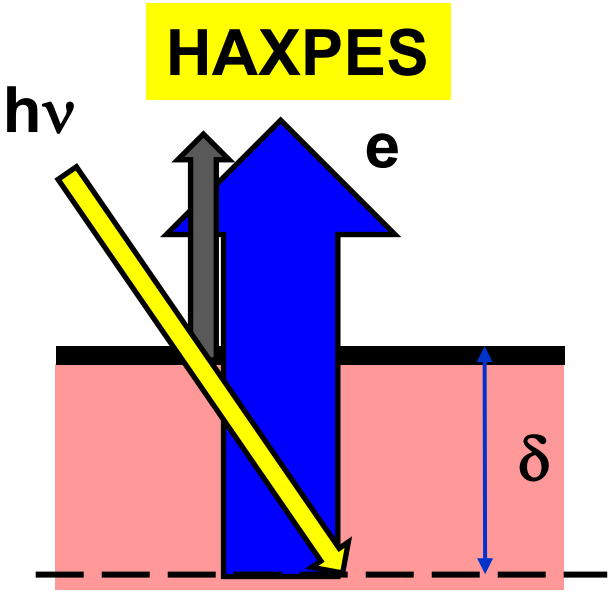
PES spectra of the Pt-CeO_2 catalyst



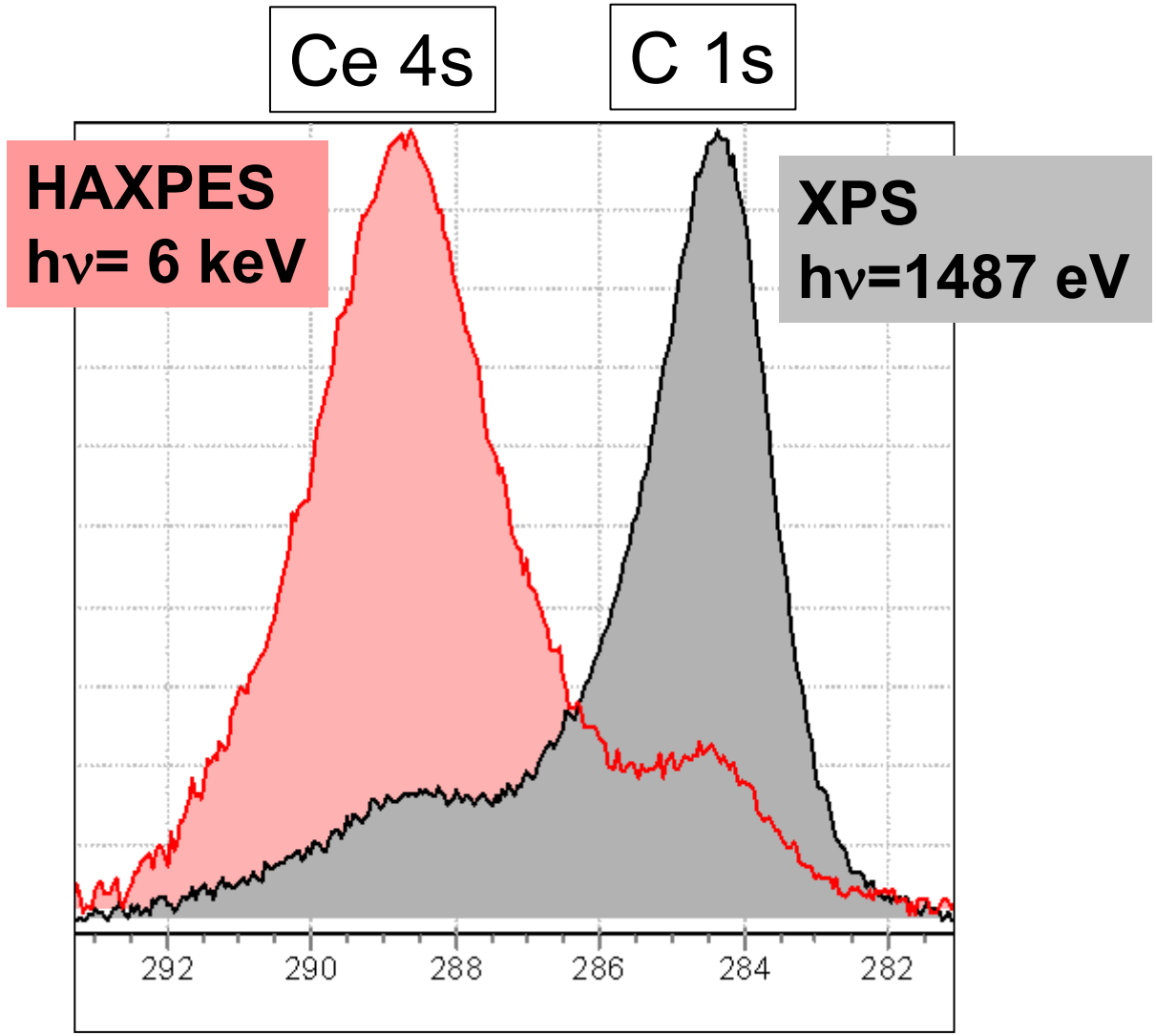


Relative Surface Sensitivity



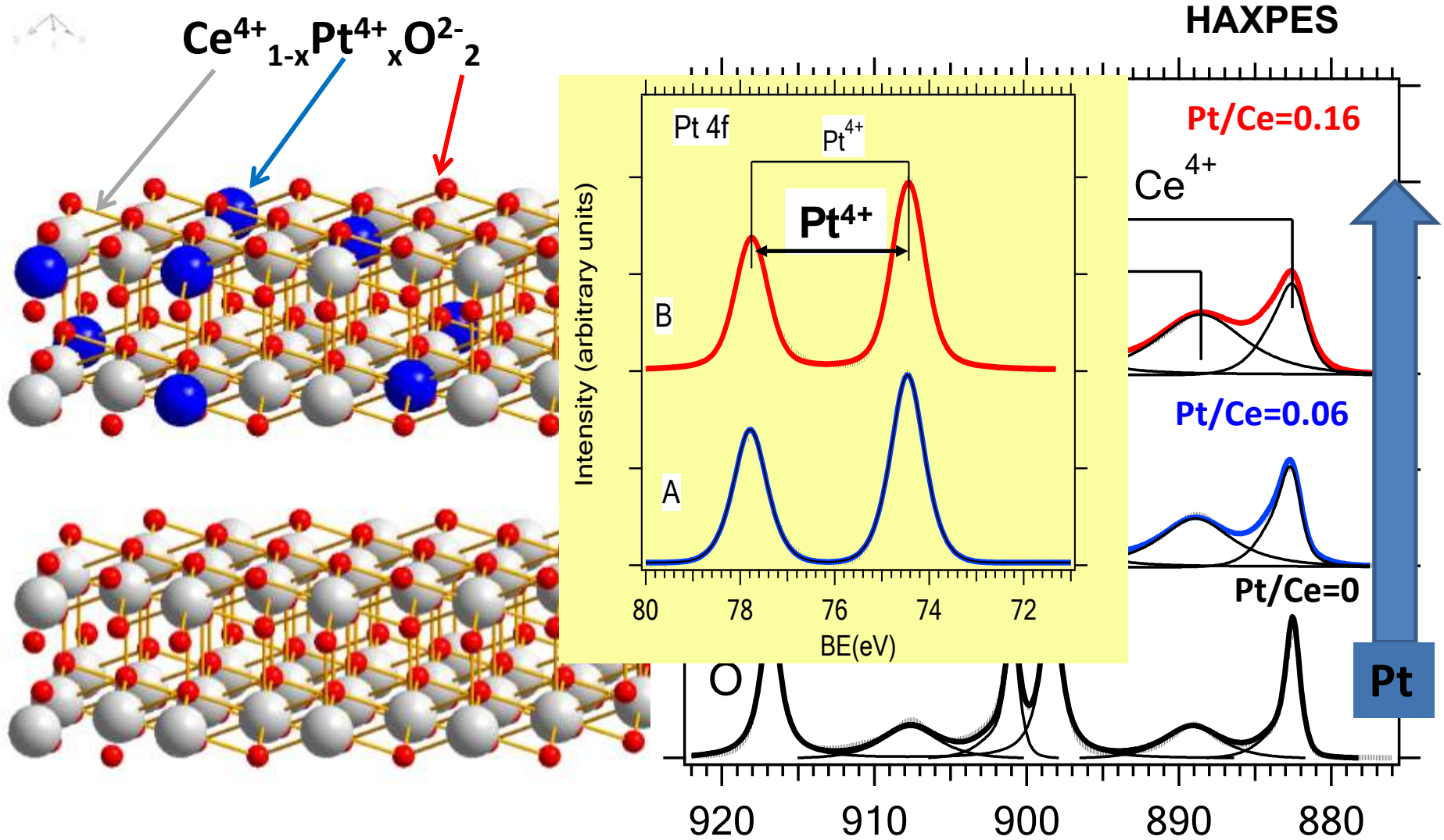


Air exposed Cerium oxide – C contamination
(normalized to peak maximum)



Co-sputtering – growth of mixed oxides (solid solution)

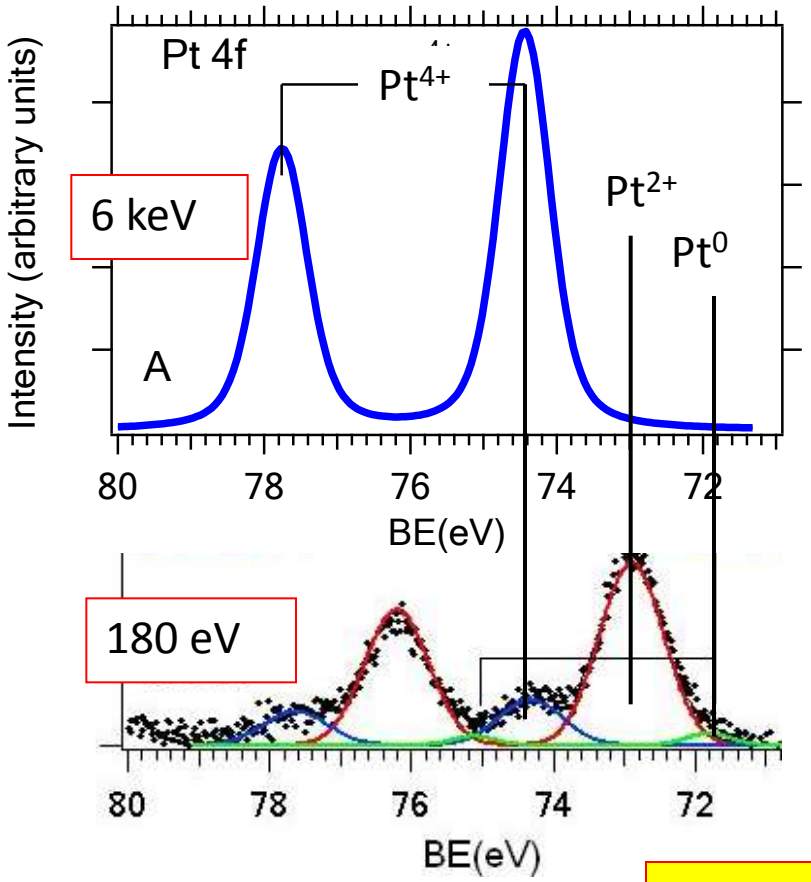
Substrate: SiO_2, normal deposition



Increase of the Ce^{4+} peak width

PES study - rf sputtered thin films: S-X→H-X

Pt-CeO_2/SiO_2/Si

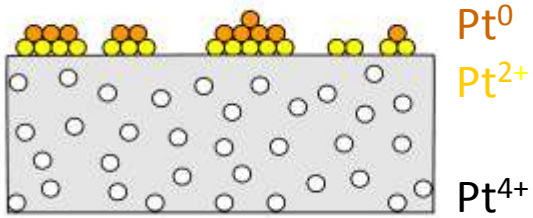


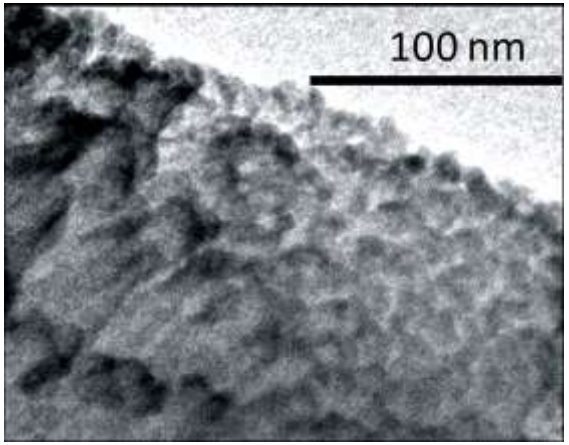
HAXPES

10 nm

SXPES

0.4 nm

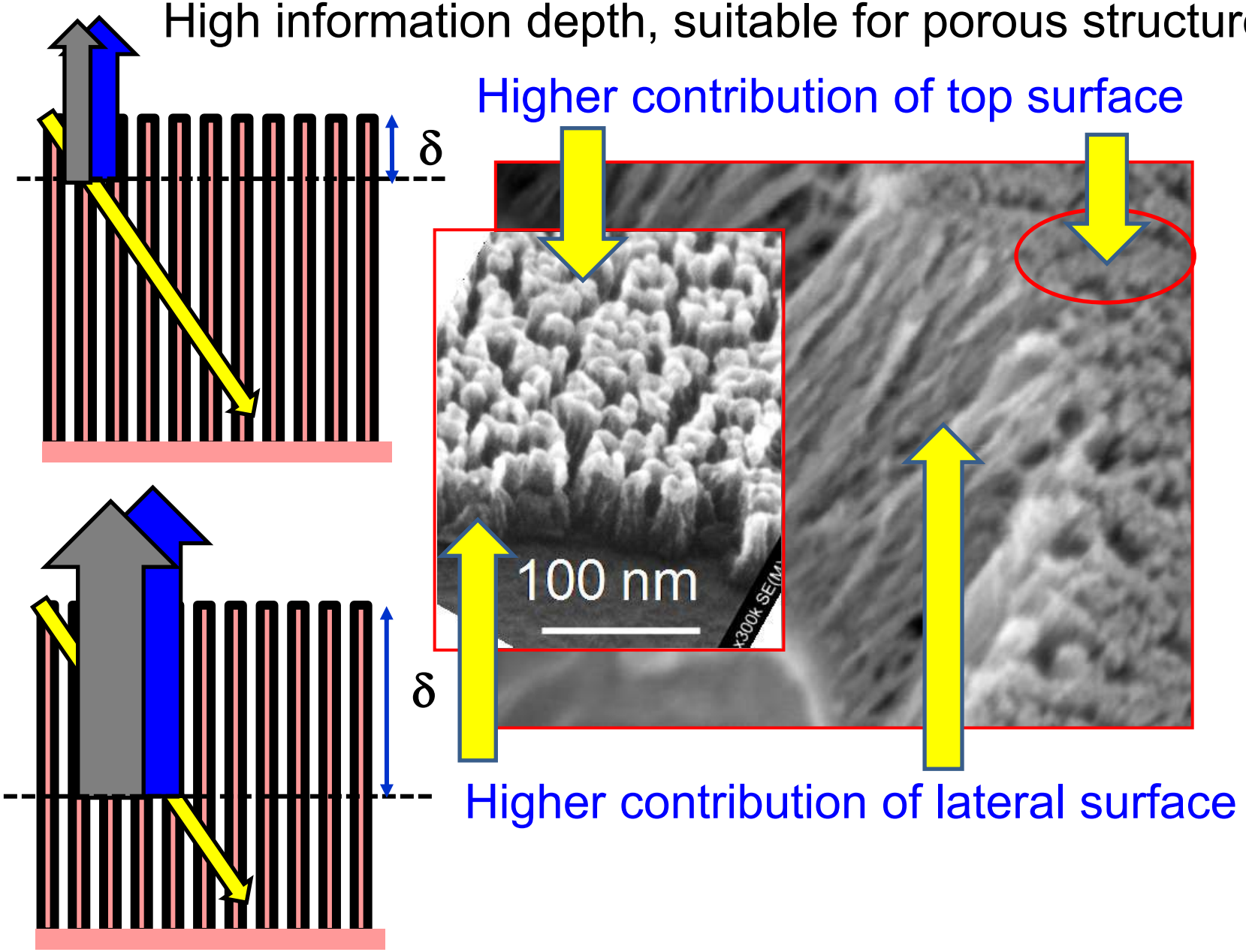


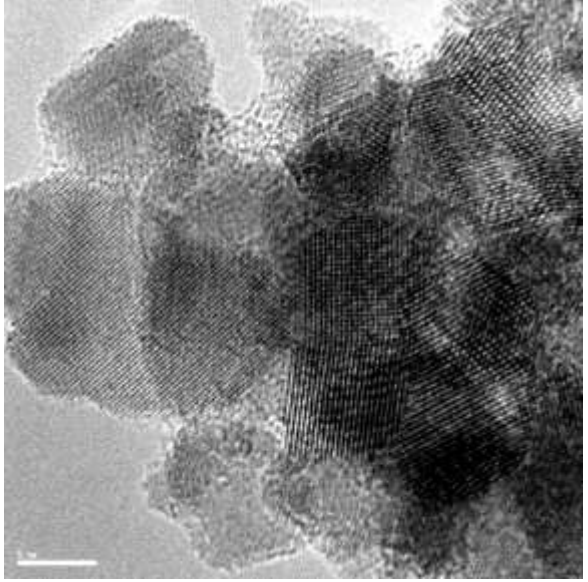


Surface is Pt^{2+} rich

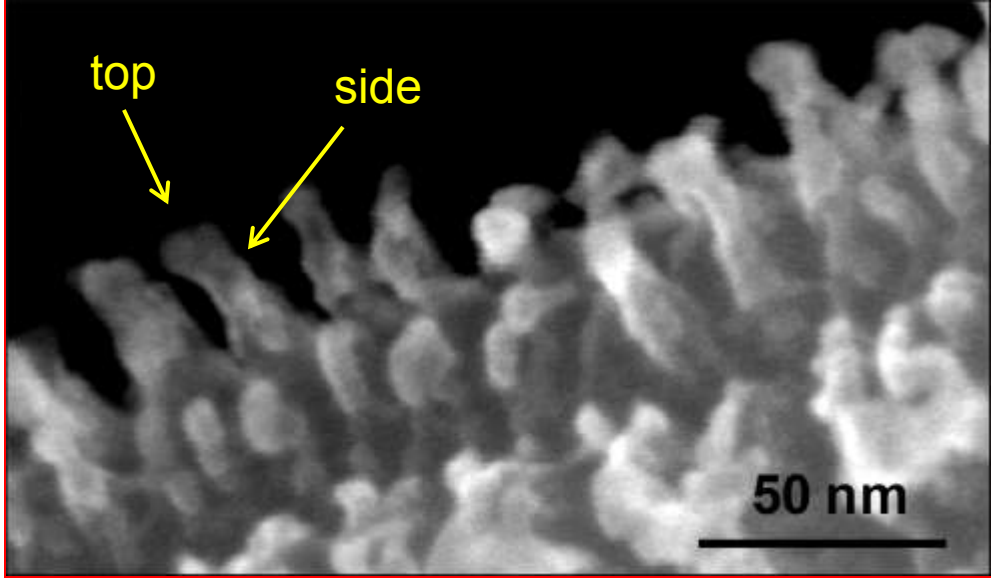
Hard X-ray Photoelectron Spectroscopy

High information depth, suitable for porous structures



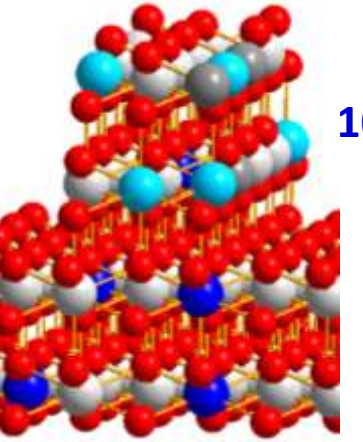


nanopowder

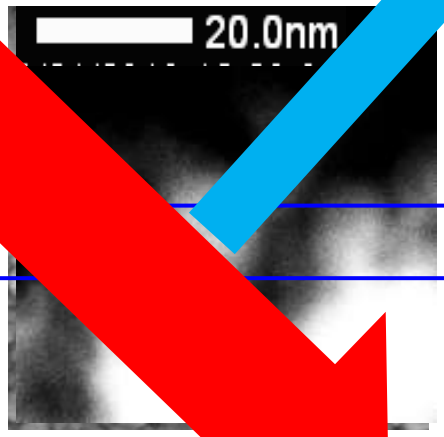


nanorods

SX→HX



10 nm



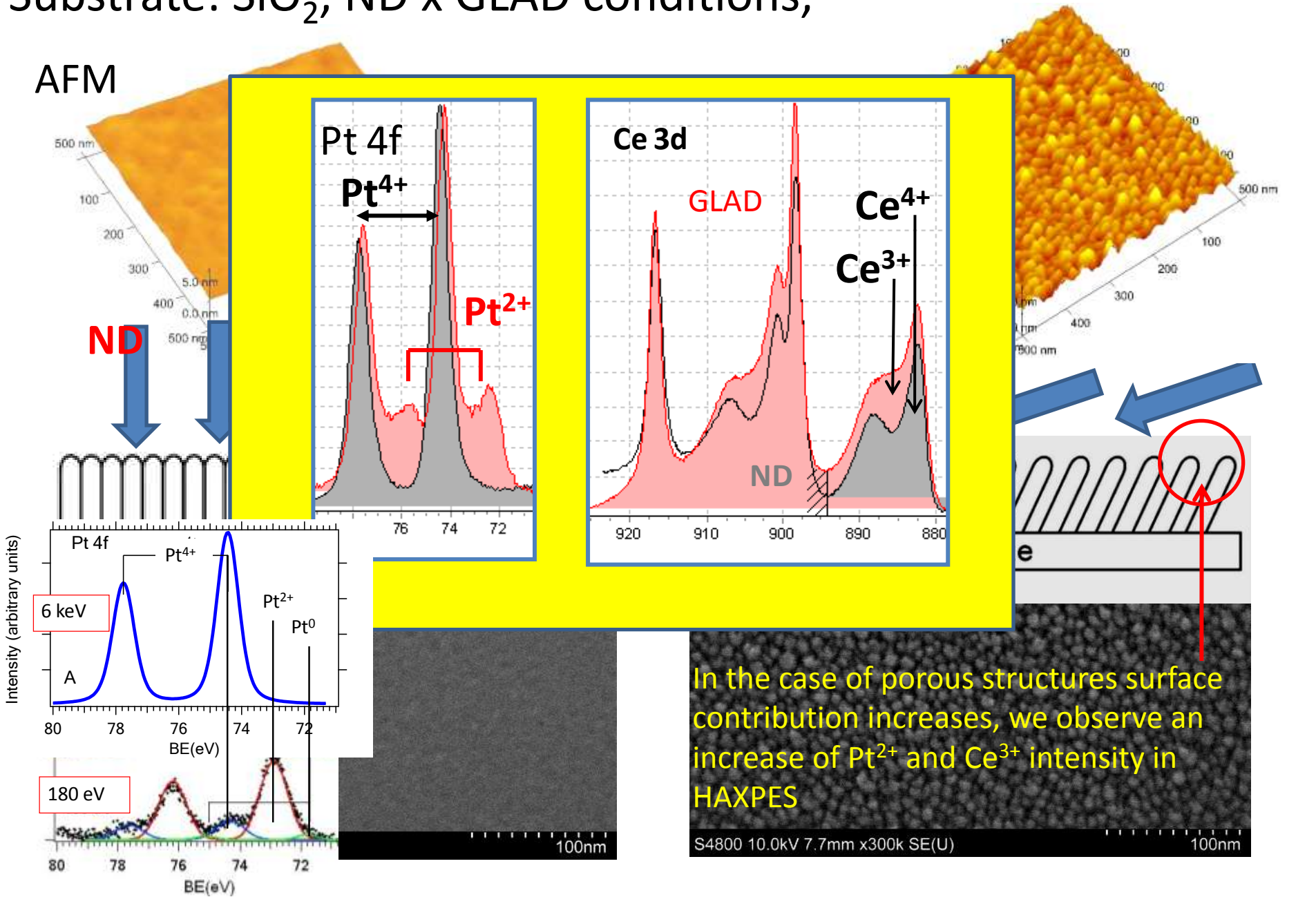
el.

Catalytic activity of top and side sites might be different due to growth mechanism

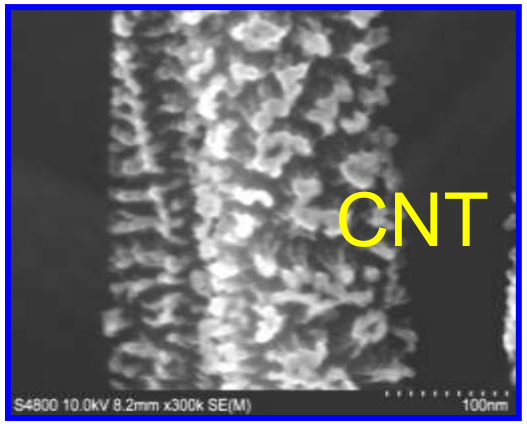
HAXPES makes possible to investigate catal. properties of in-pore catalytic sites

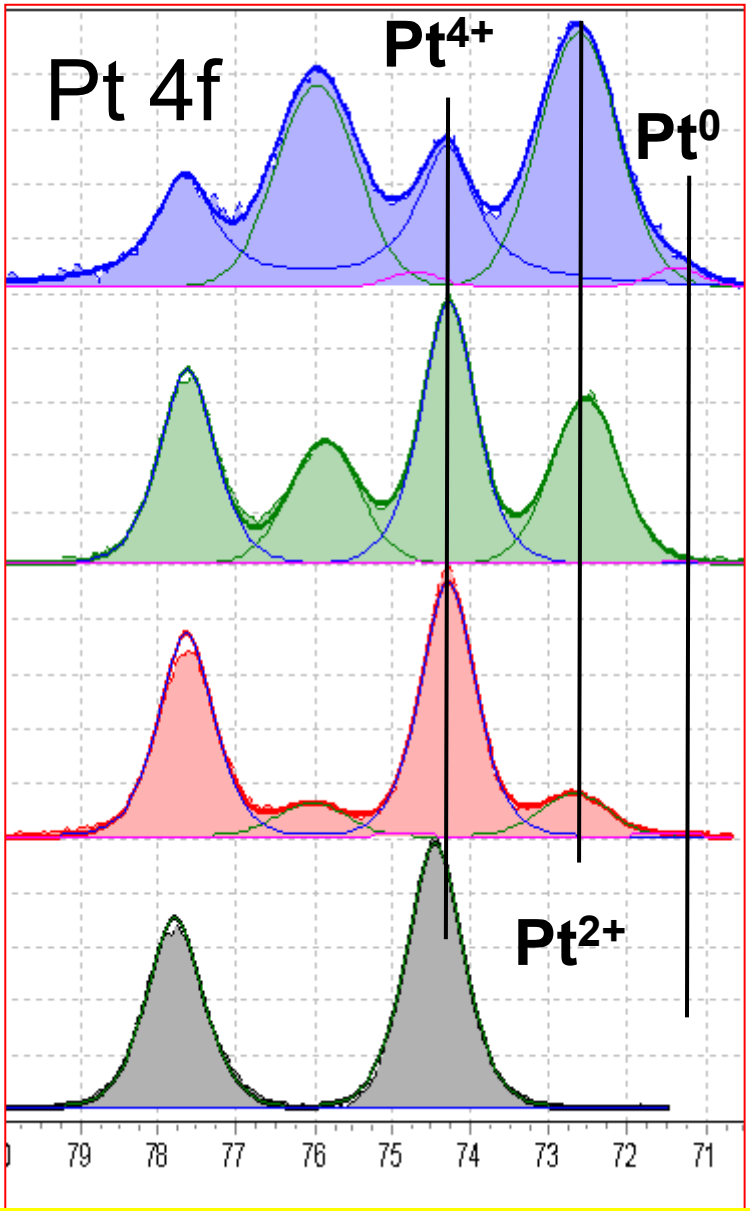
Co-sputtering – growth of mixed oxides (solid solution)

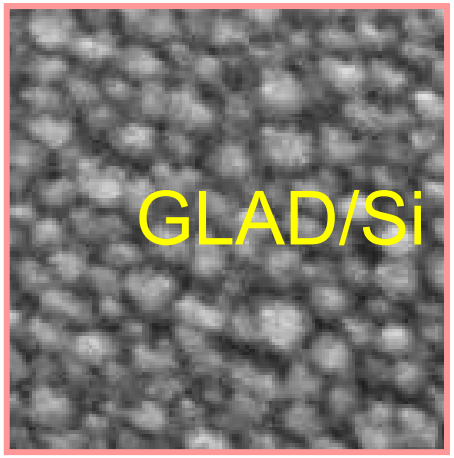
Substrate: SiO_2, ND x GLAD conditions,

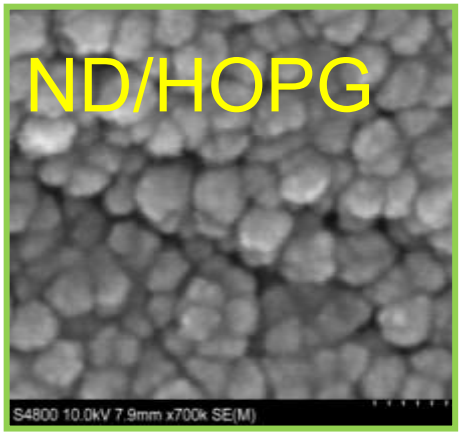


Morpholgy-substrate determined chemical state of Pt



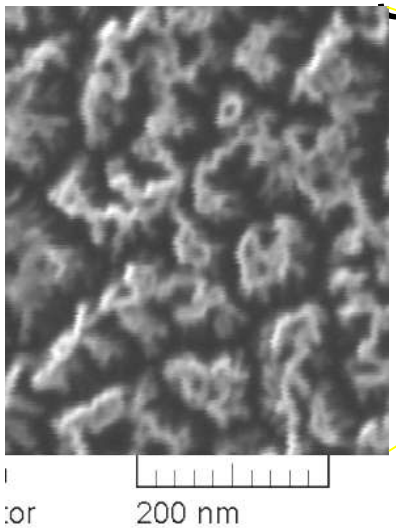


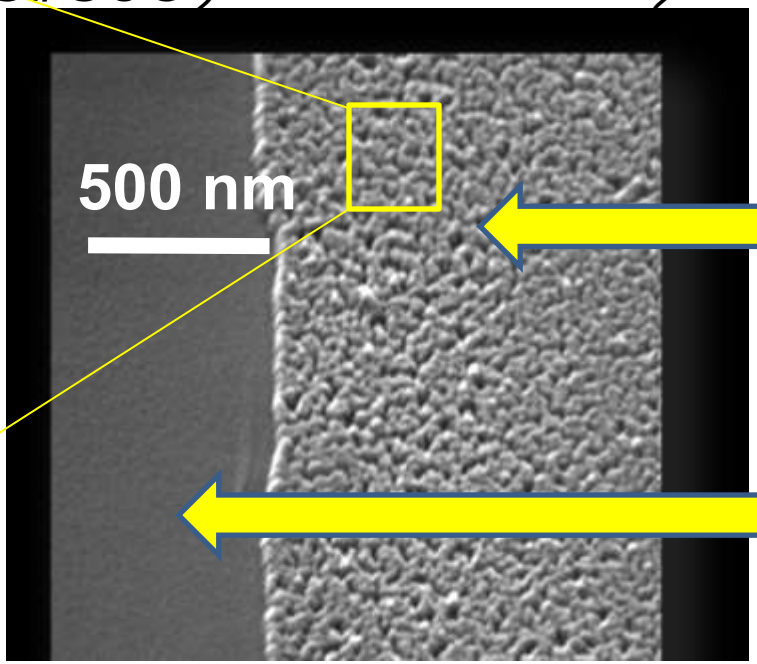


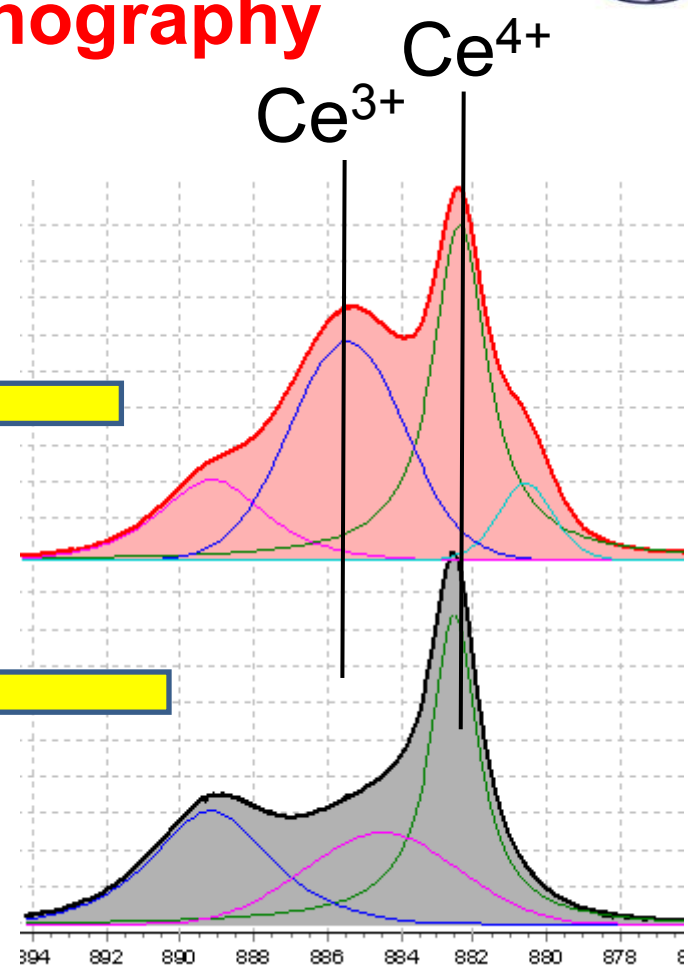


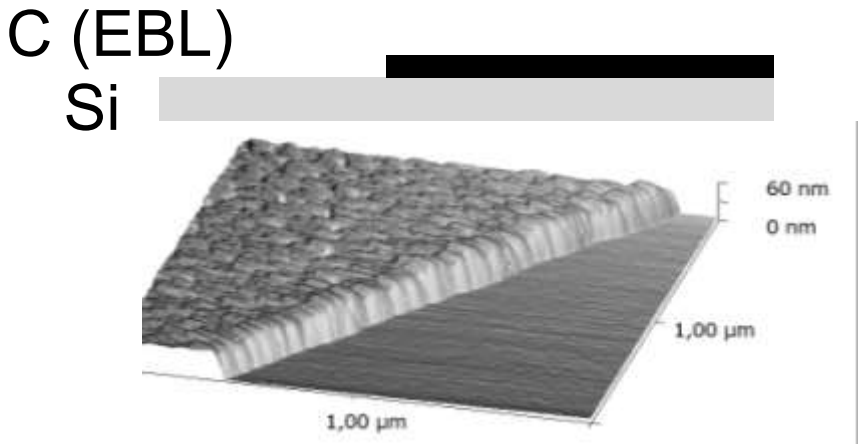
WHY POROUS FILMS ARE GROWN ON C???

CeO_2 growth on 5 nm sputtered carbon film prepared by electron beam lithography

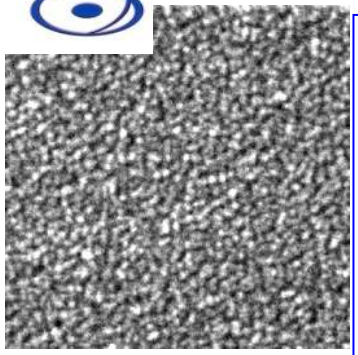


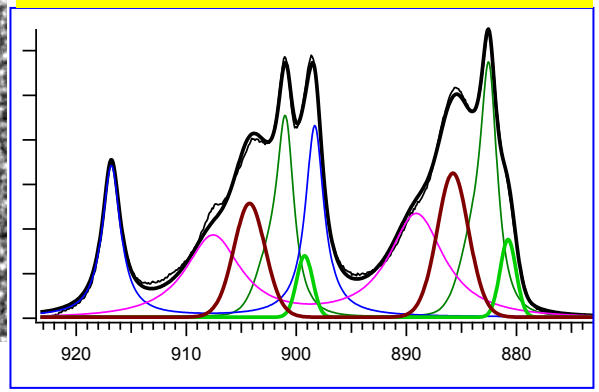




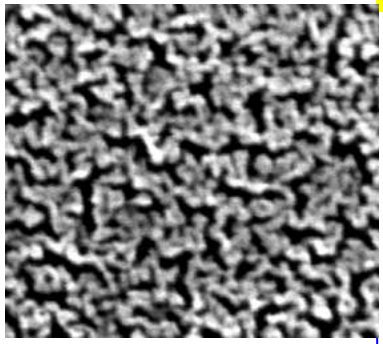


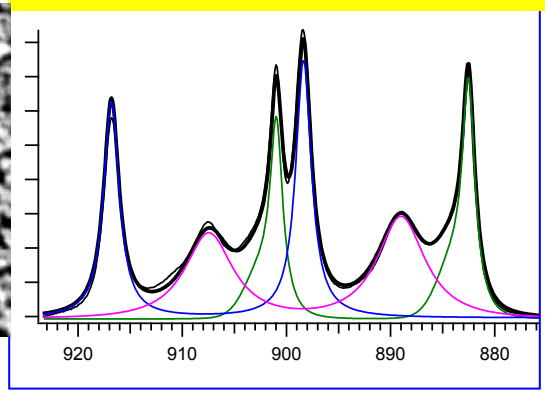
1.5 nm Ce^{3+}/Ce = 0.23



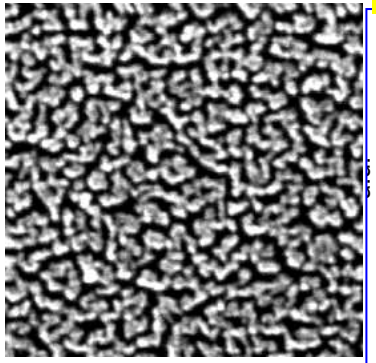


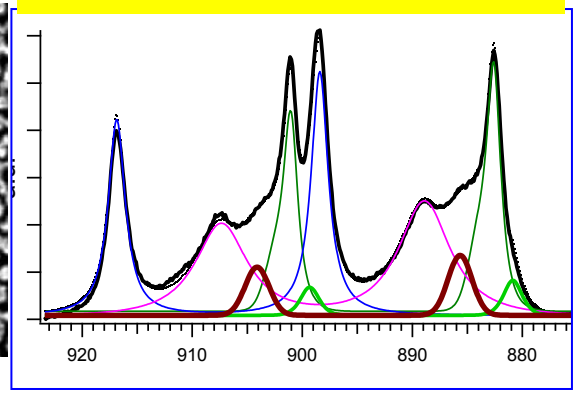
9 nm, Ce^{3+}/Ce = 0.02



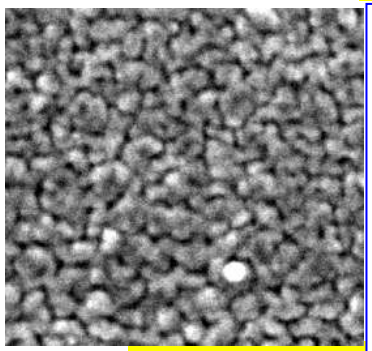


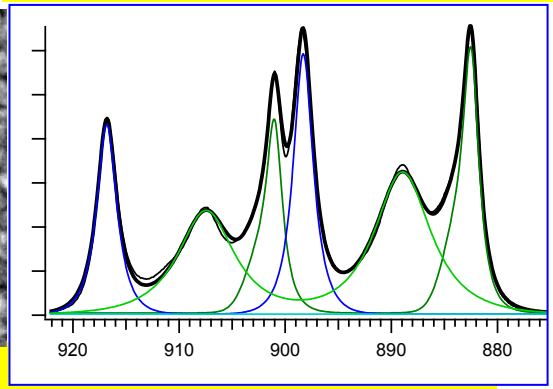
3 nm, Ce^{3+}/Ce = 0.10



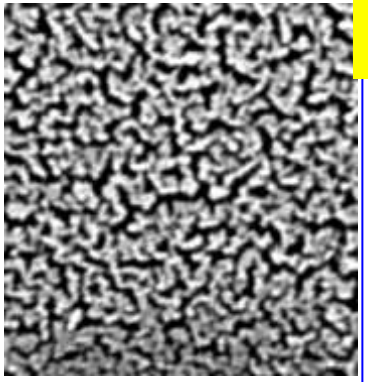


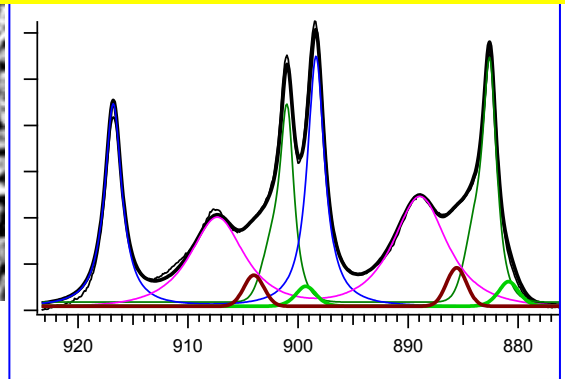
18 nm, Ce^{3+}/Ce = 0

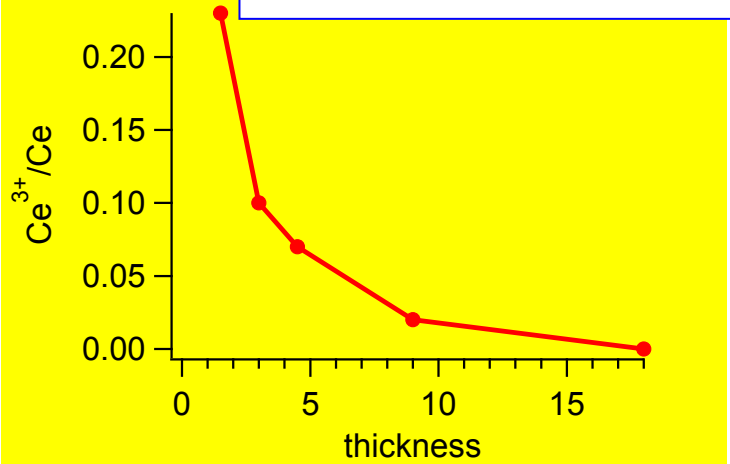




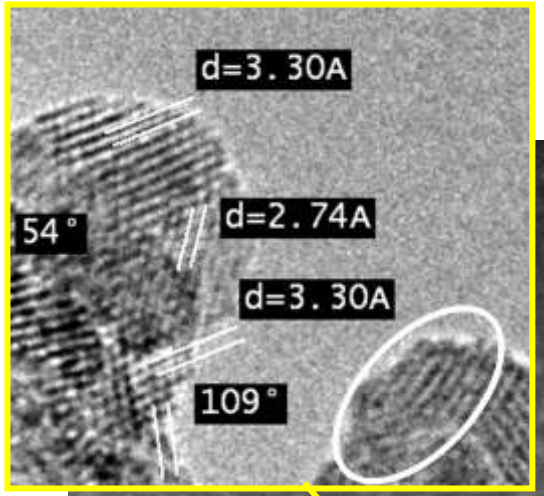
4.5 nm, Ce^{3+}/Ce = 0.07



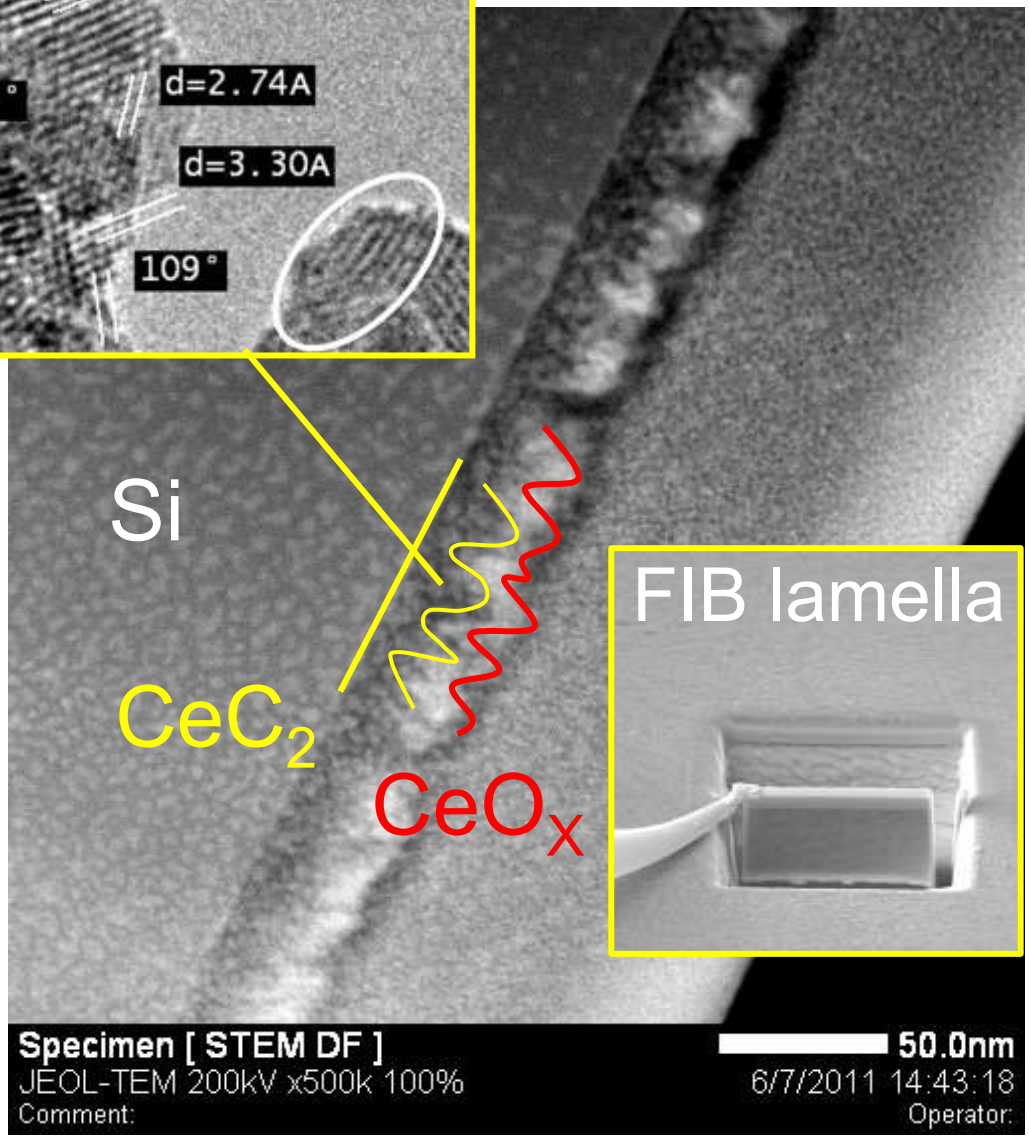




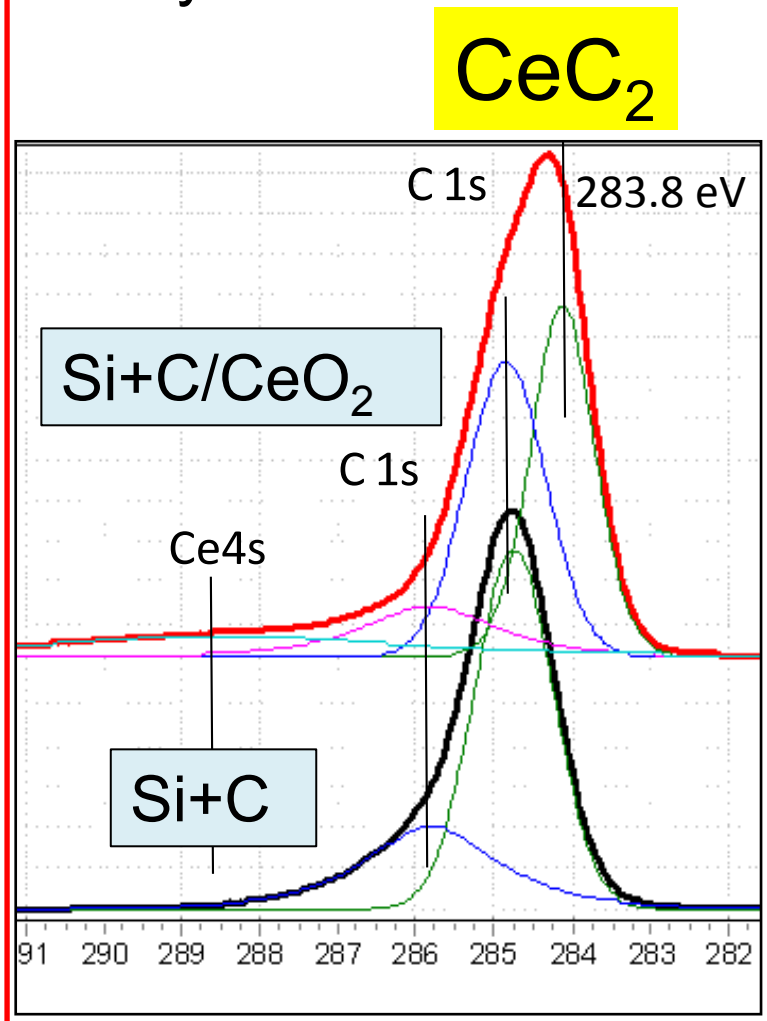
HRTEM: CeC_2 zone axes

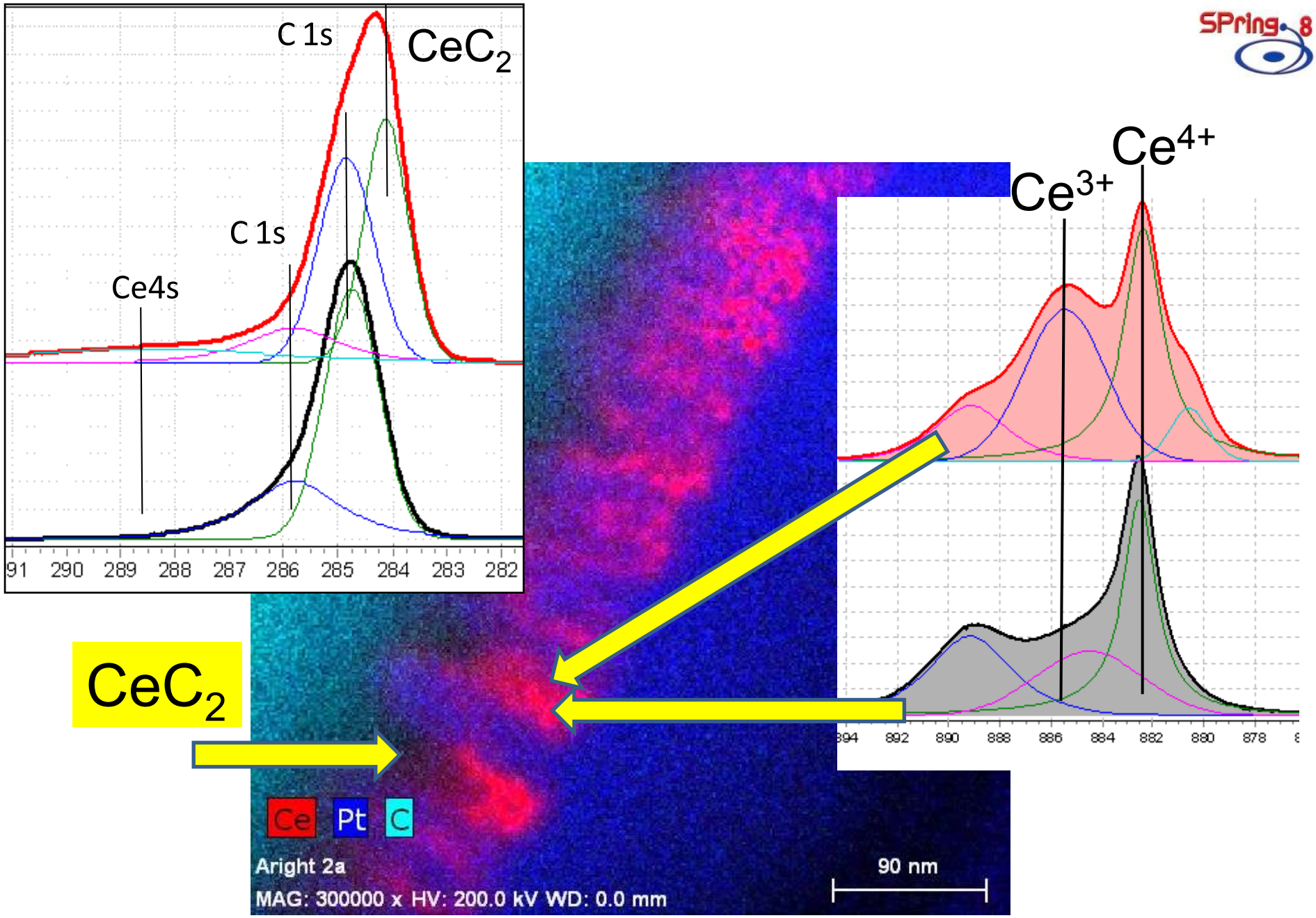


S-TEM: interface observation

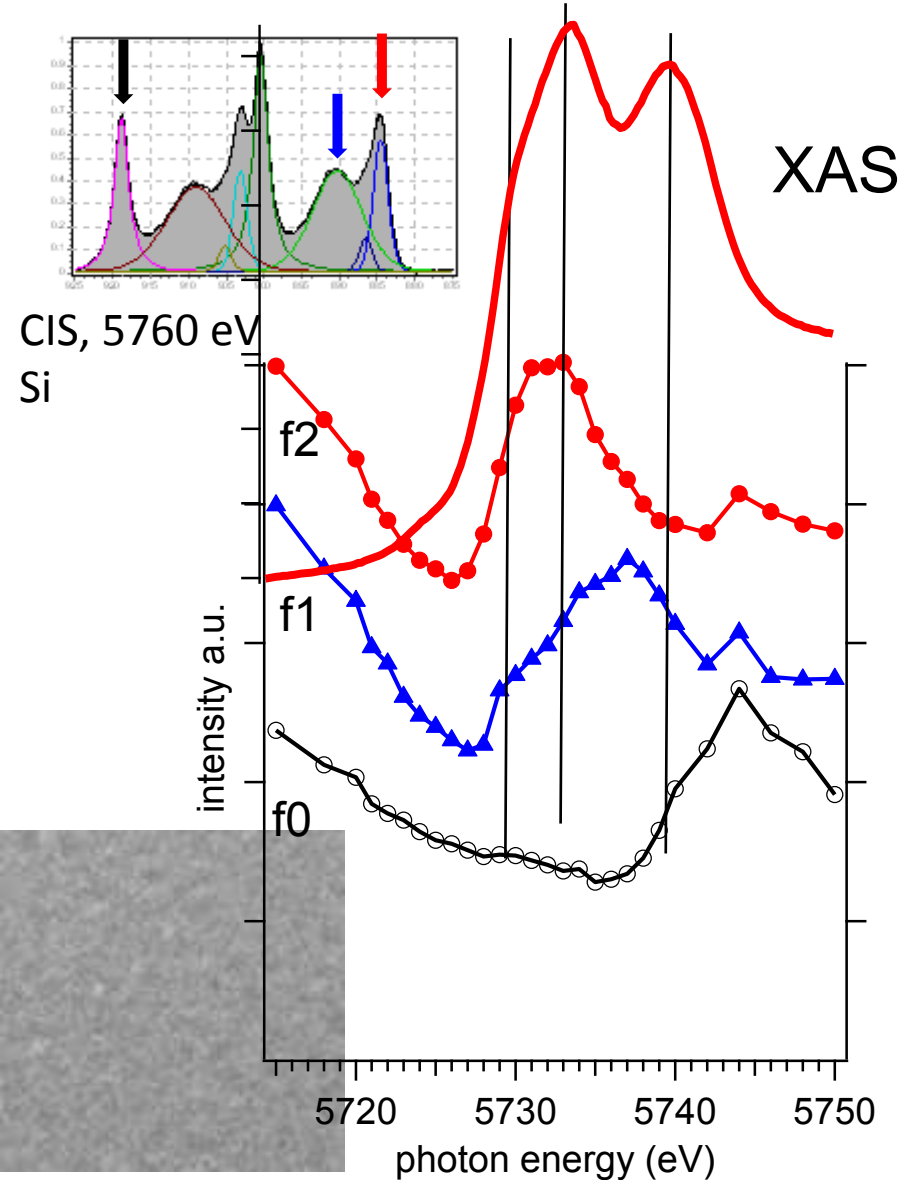


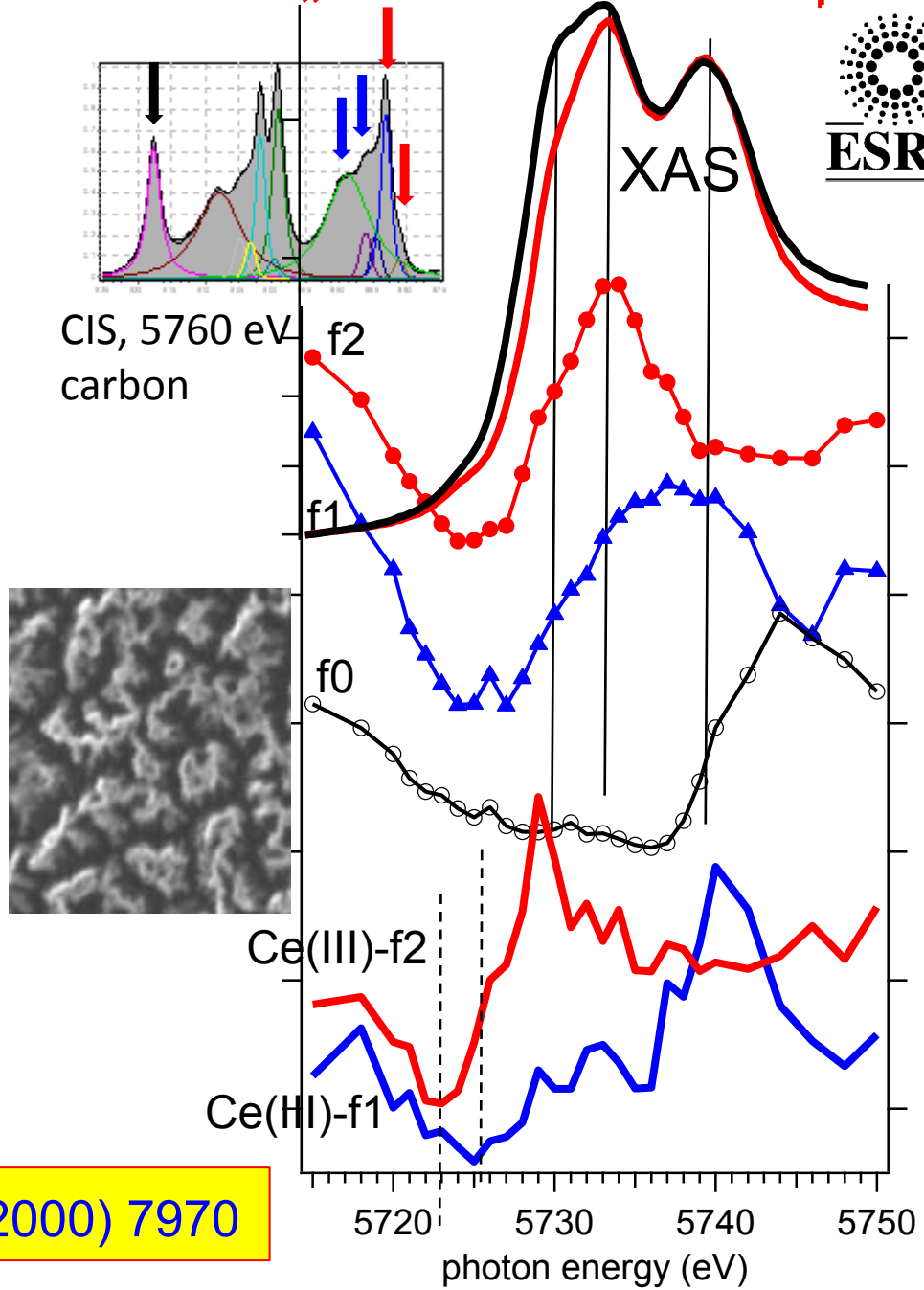
HAXPES interface analysis: C 1s




C 1s
CeC_2
C 1s
Ce4s
291 290 289 288 287 286 285 284 283 282
Ce^{4+}
Ce^{3+}
894 892 890 888 886 884 882 880 878
CeC_2
Ce
Pt
C
Aright 2a
MAG: 300000 x HV: 200.0 kV WD: 0.0 mm
90 nm

Future prospects: use of associated „volume“ techniques





XAS and Ce L_3 RPES, PRB 62 (2000) 7970

Co-operations:

Spring-8 BL15XU-NIMS: H. Yoshikawa, K. Kobayashi, S. Ueda

ESRF ID32: B. Detlefs, Univ. Bourgogne: S. Bourgeois, V. Potin

Surface Science Group of the Dpt. Surface and Plasma Science, CU

Professors and researchers:

Viktor Johánek
Jiří Libra
Karel Mašek
Iva Matolínová
Václav Nehasil
Kateřina Veltruská
Josef Mysliveček
Daniel Mazur

Surface Analysis

PhD Students:

Miloš Cabala
Michal Škoda
Břetislav Šmíd
Michal Václavů
Roman Fiala
Mykhailo Vorokhta
Igor Píš
Ivan Khalakhan
Mykhailo Chundak
Oleksander Stetsovych
Stanislav Haviar
Filip Dvořák
Jan Beran

PhD Students:

Táňa Záhoranová
Klara Ševčíková
Lucie Szabova
Andrei Rednik
Petr Blumentrit

MS Beamline@Elettra, Trieste, Italy:

Tomáš Skála
Natalia Tsud