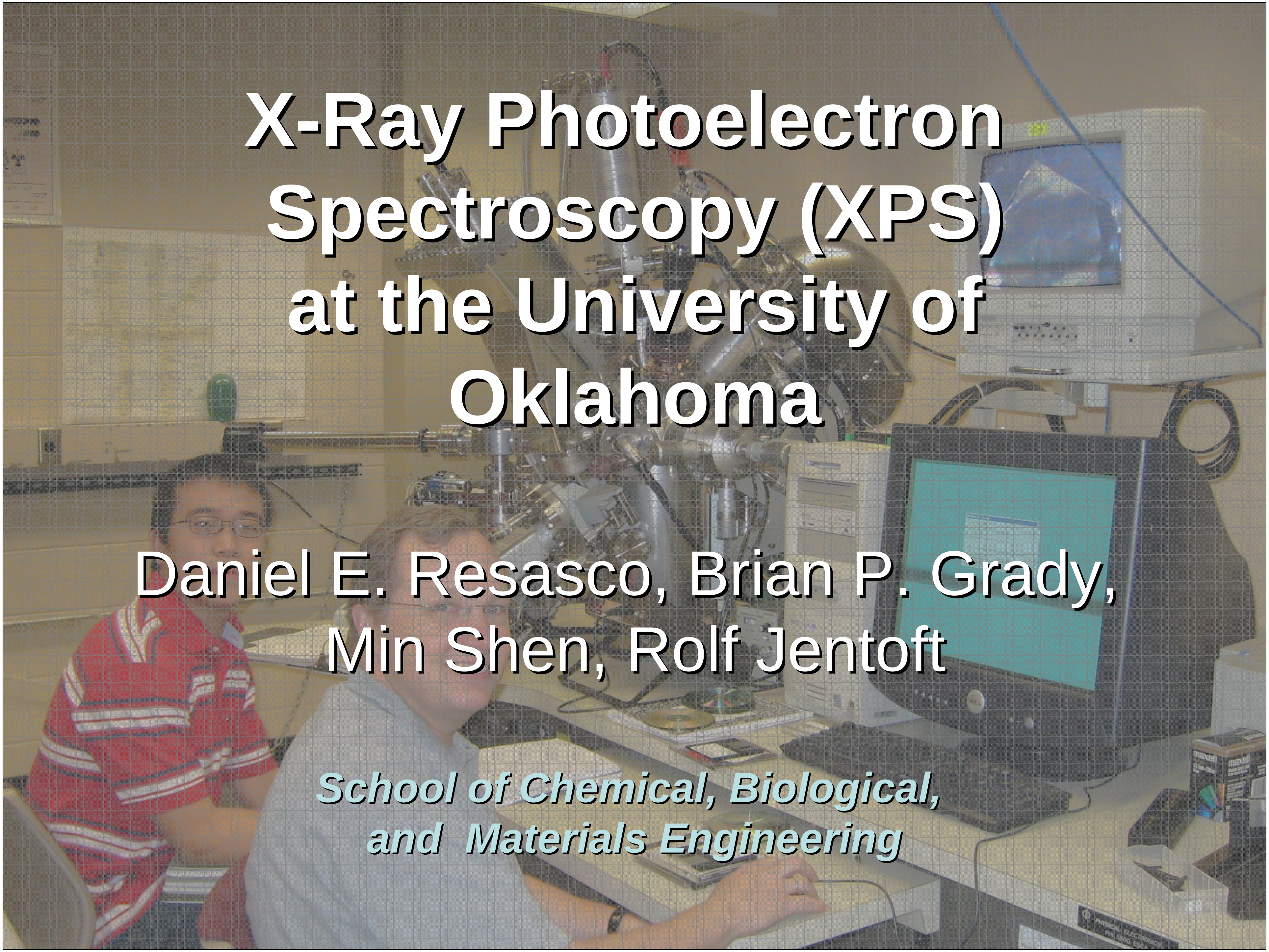

X-Ray Photoelectron Spectroscopy (XPS) at the University of Oklahoma

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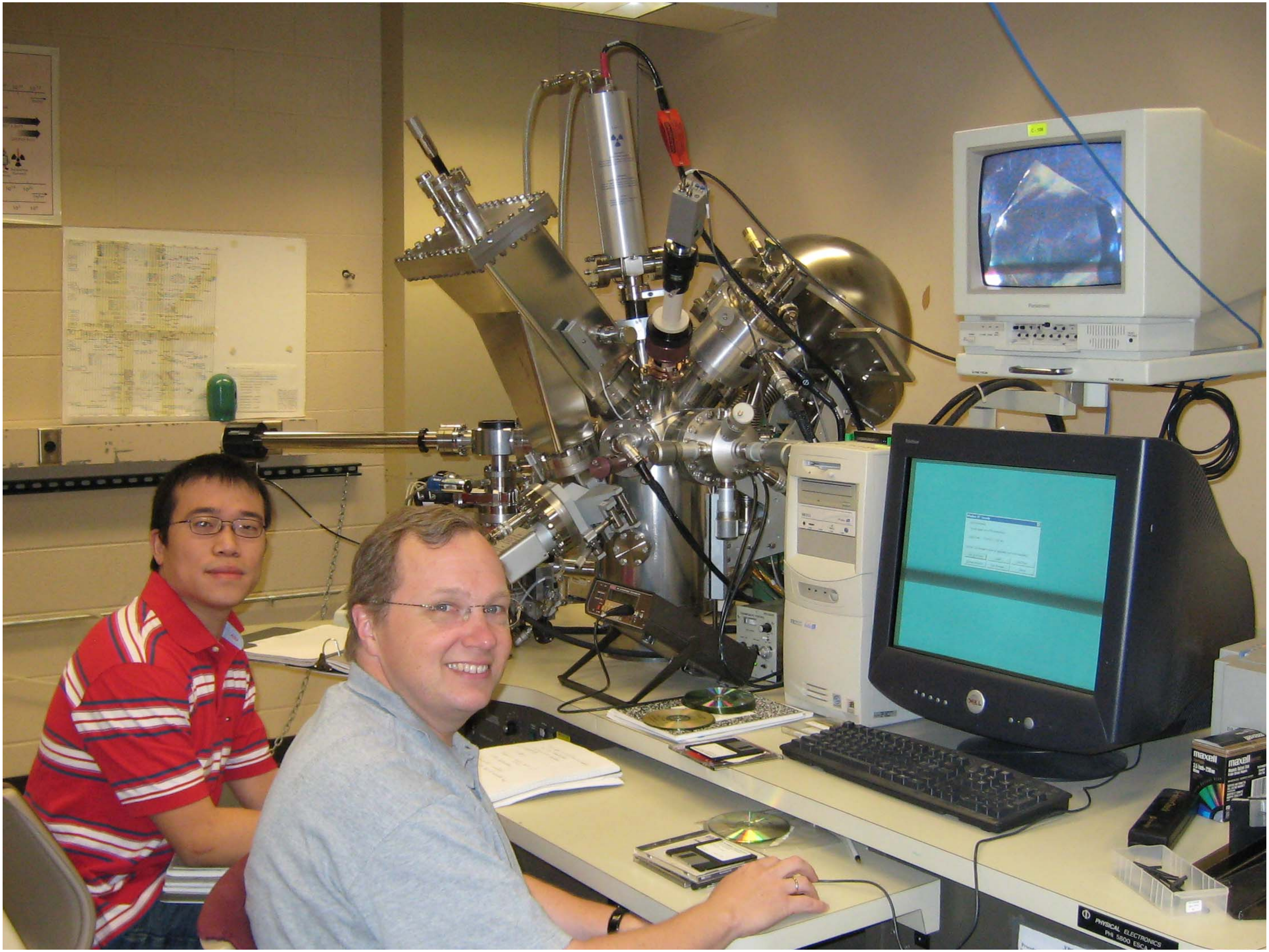
Min Shen, Rolf Jentoft

*School of Chemical, Biological,
and Materials Engineering*

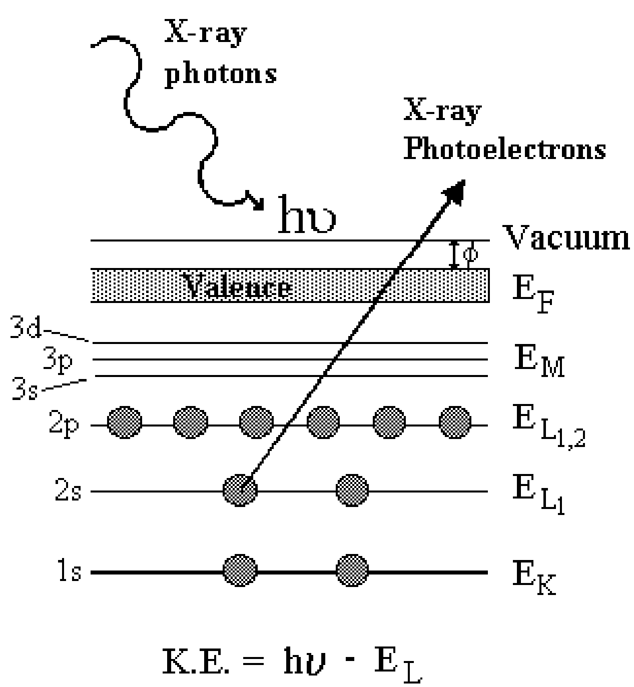

PHYSICAL ELECTRONICS
PHI 5800 ESCA
maxell

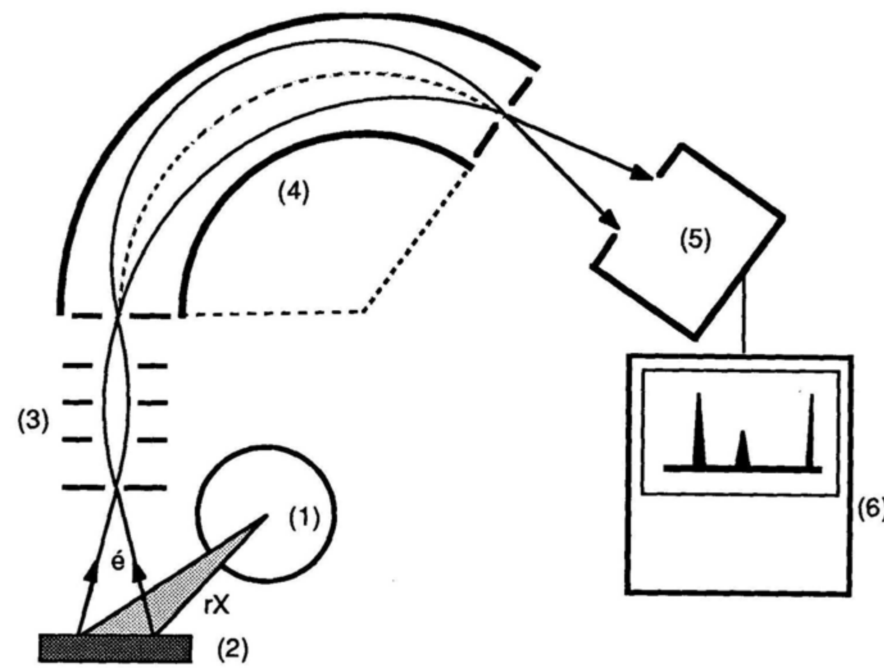
X-Ray Photoelectron Spectrometer (XPS)

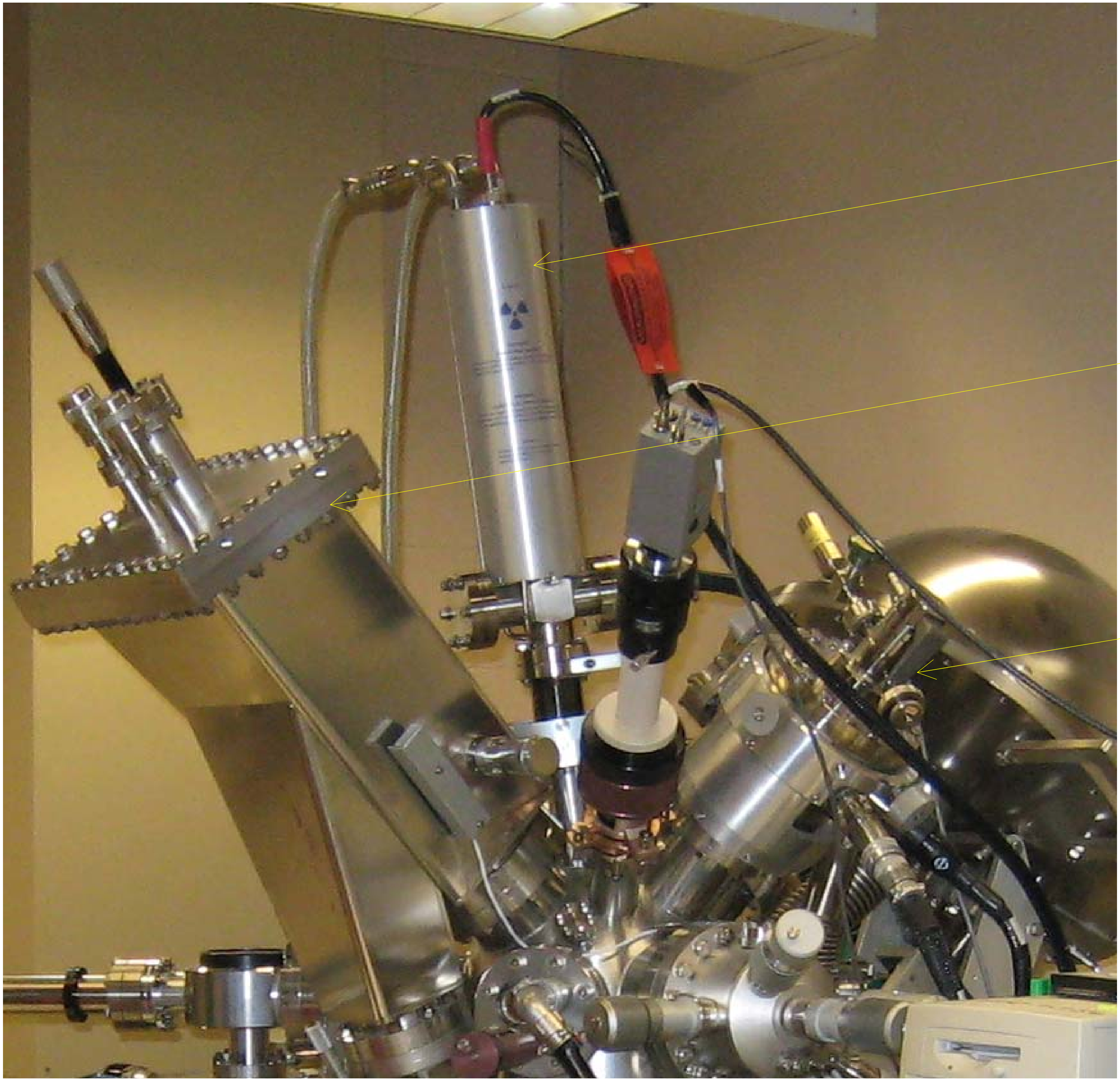
XPS measures electrons emitted at an energy according to their binding energy.

Each chemical element is characterized by a single spectrum

XPS makes it possible to analyze chemical composition of surface and identify its chemical state.



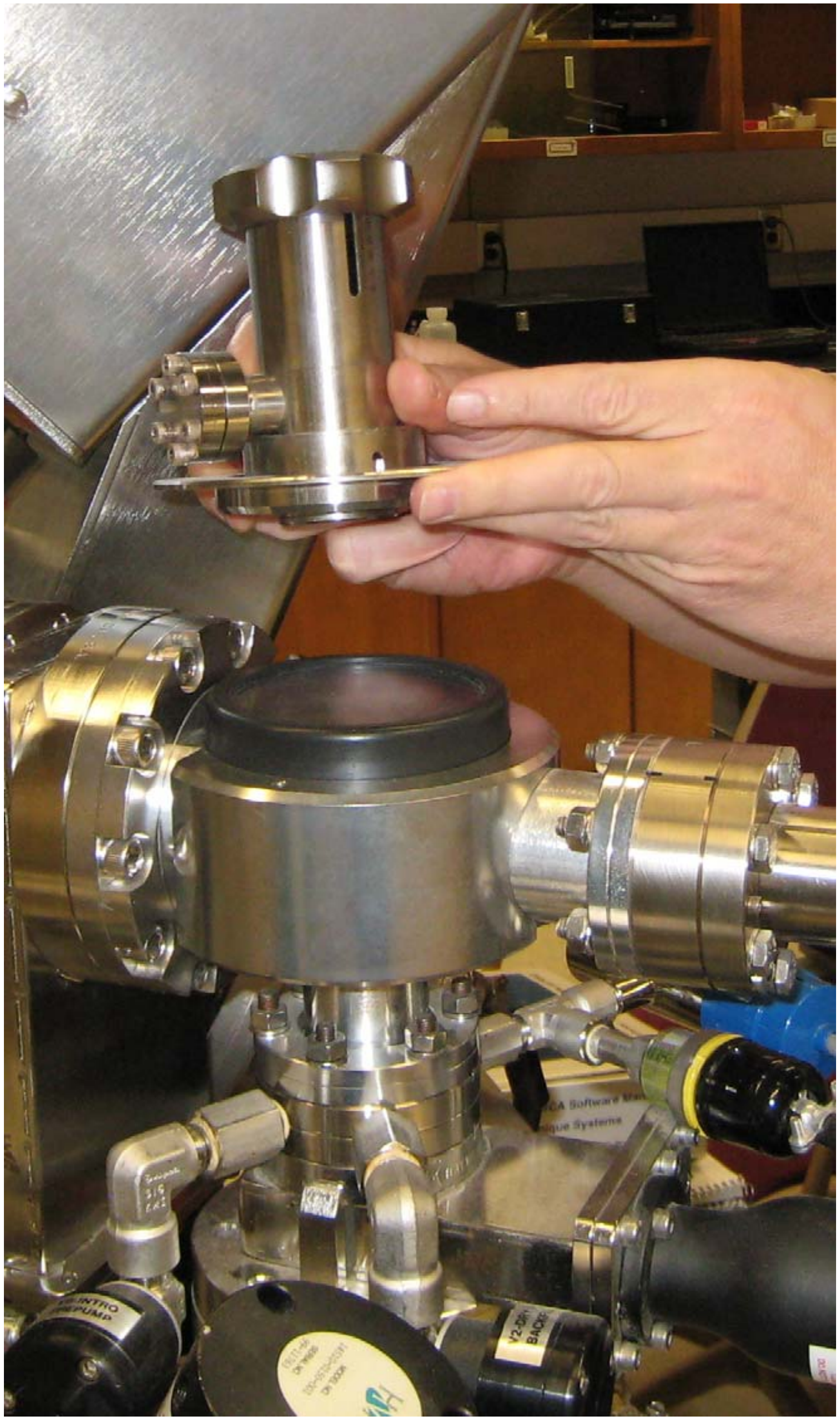




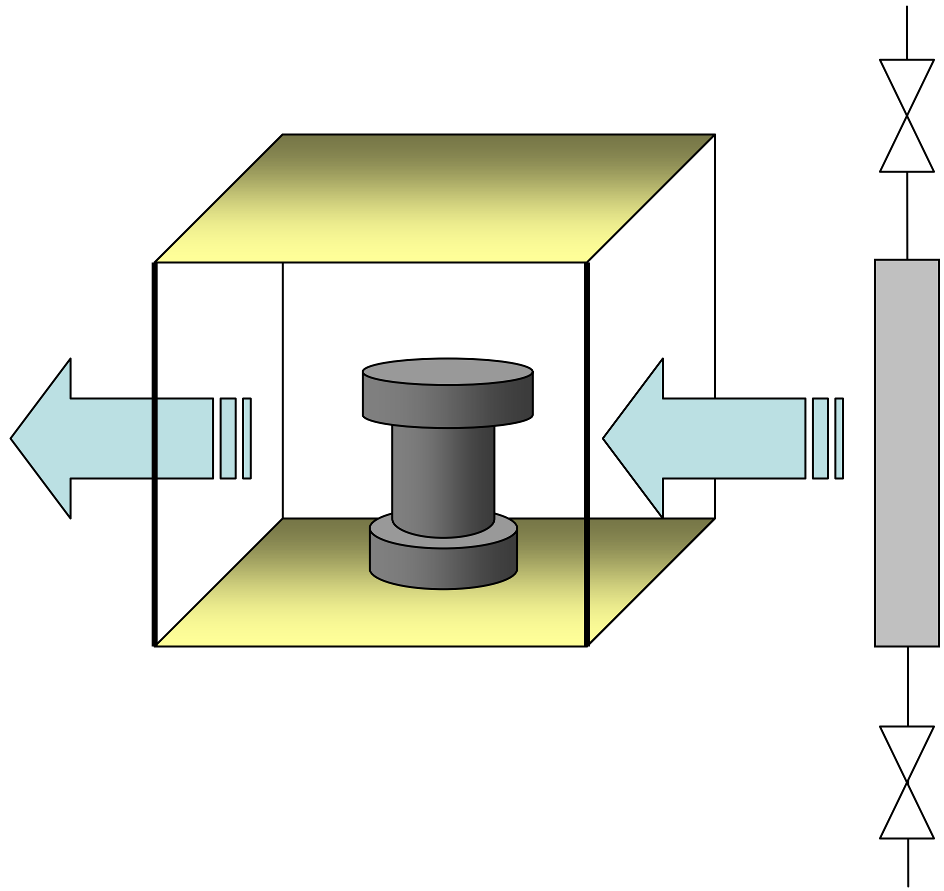
Dual Anode X-ray source

Monochromatic Radiation Source

Argon Ion Gun

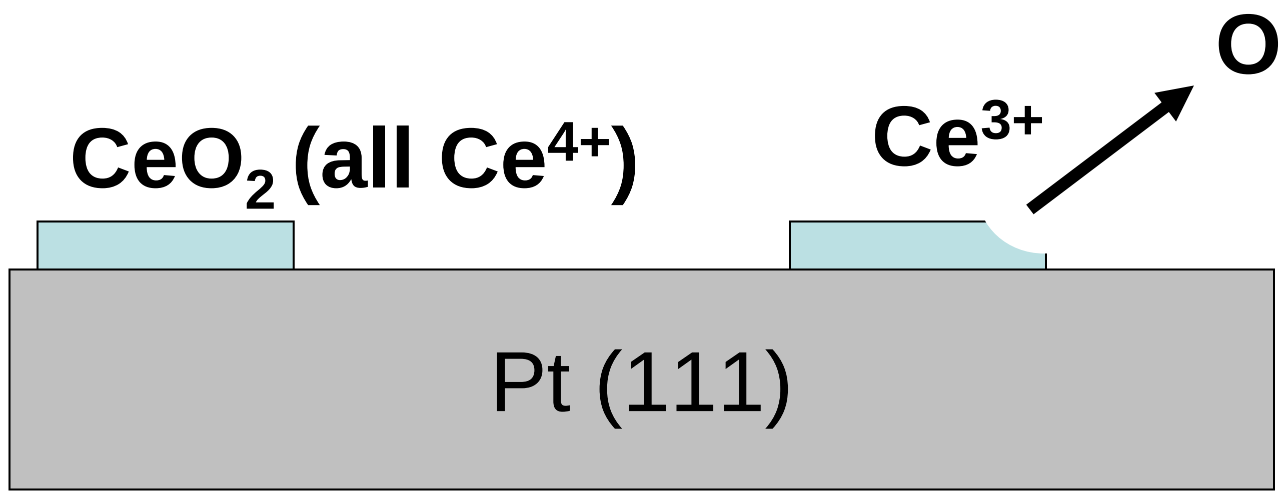


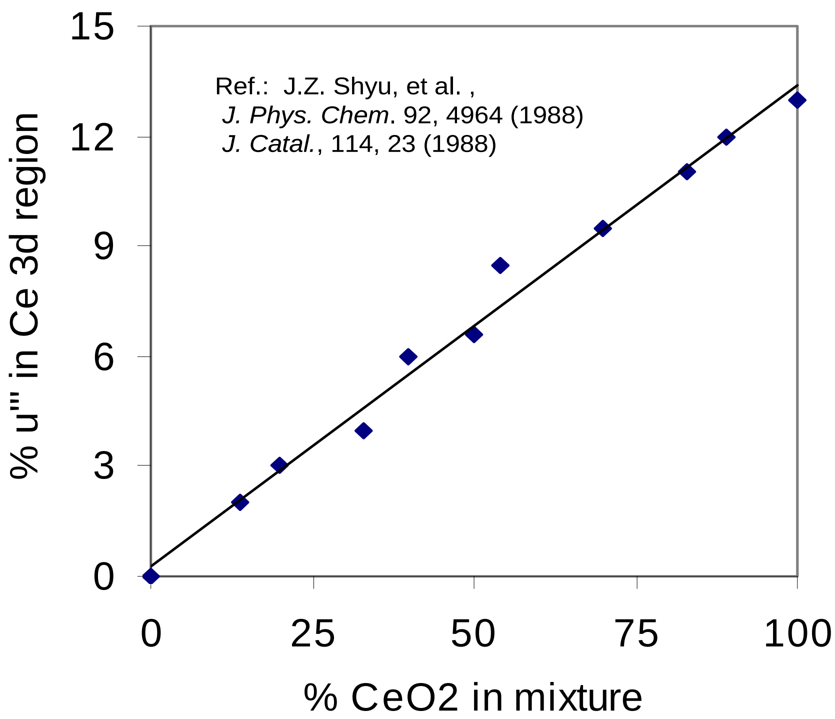
Gas-tight transfer cell for ex-situ reactions

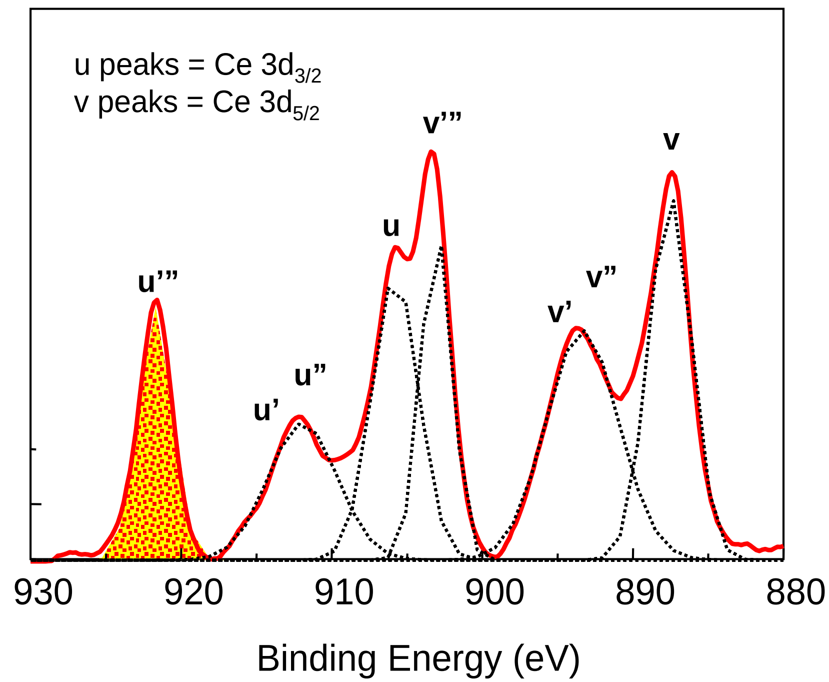


Example 1: Oxidation State of Ce under reaction conditions (CO_2 + CH_4 reaction)

- **If Ce oxide is stoichiometric, (that is, no O vacancies) then 100 % as Ce^{4+}**
- **If vacancies are formed, then Ce^{3+}**





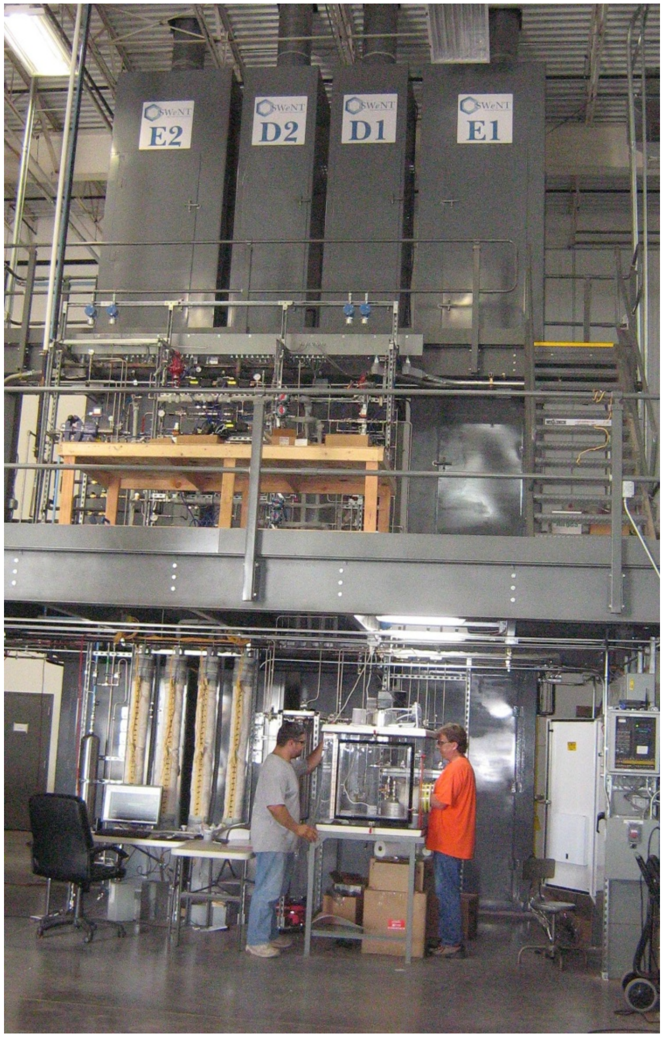


Under reaction conditions two reactions occur:

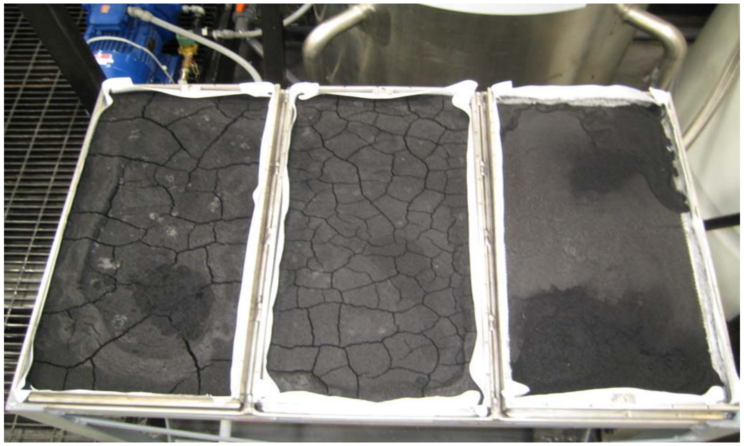
- Ce^{4+} to Ce^{3+}
  by reduction with CH_4
- Ce^{3+} to Ce^{4+}
  by oxidation with CO_2

Pretreatment	% Ce^{4+}
Oxidation in O_2 at 760C	100 %
Reaction $CH_4:CO_2 = 1:1$	82 %
Reduction in CO at 760C	65 %
Reaction $CH_4:CO_2 = 1:1$	83 %

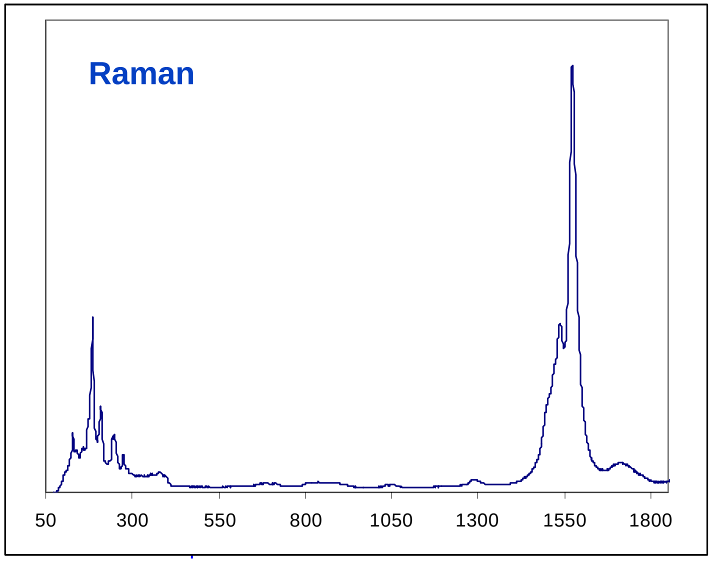
<u>Example 2</u>: Single-walled carbon nanotubes

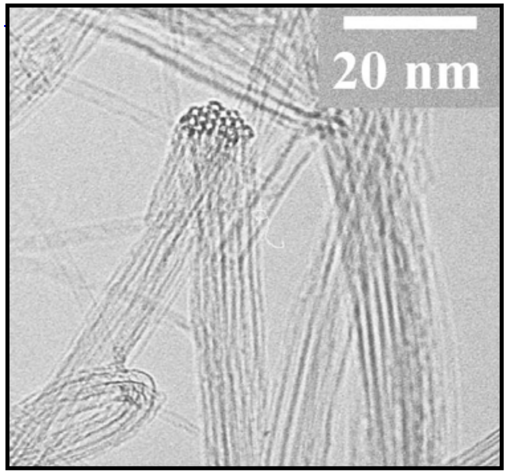


Large-scale production of High-quality SWNT



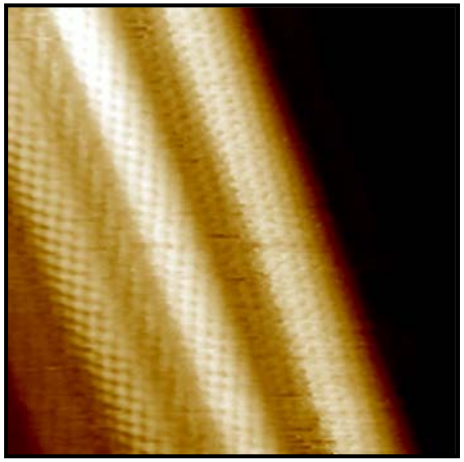
The CoMoCAT product

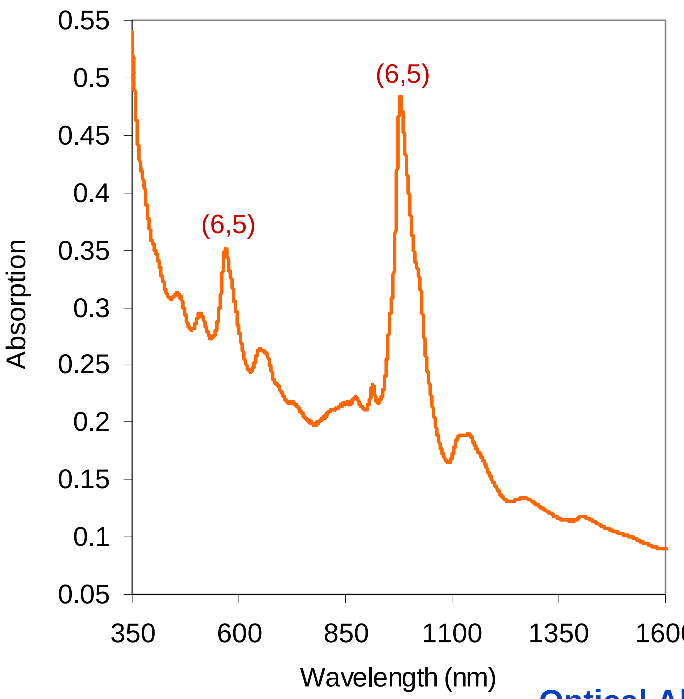




TEM

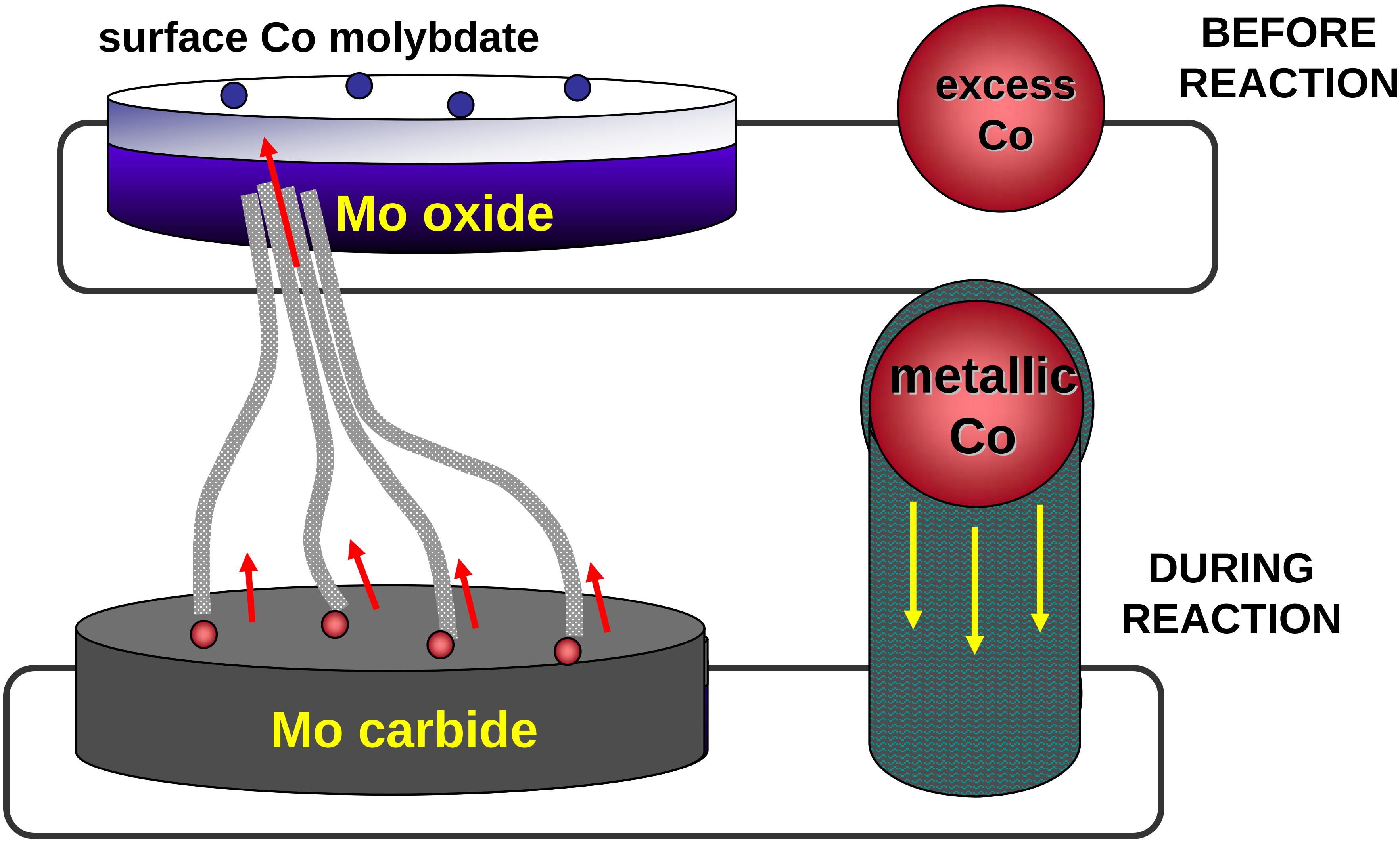
STM



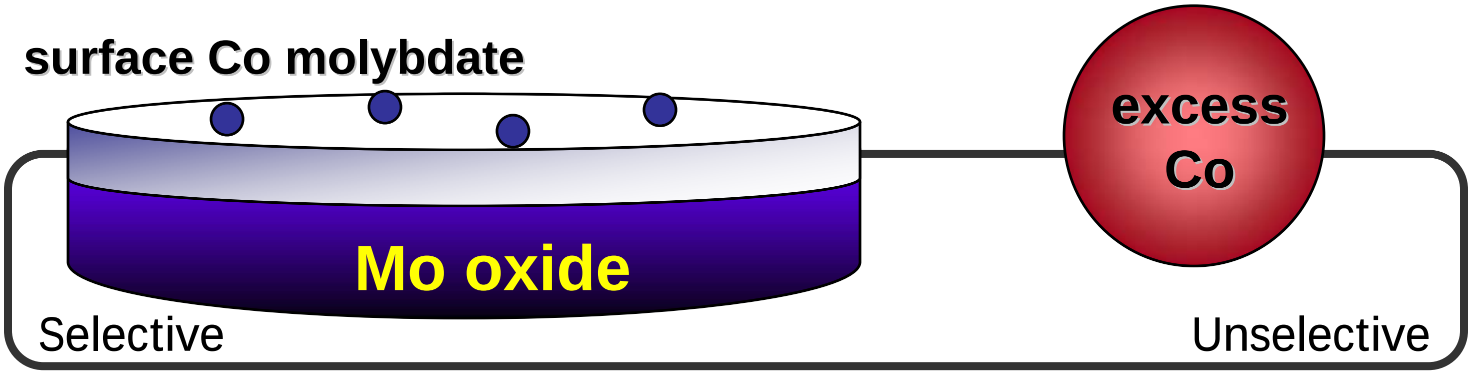


Optical Absorption

Example 2: Co-Mo catalysts for nanotube synthesis (SWNT)

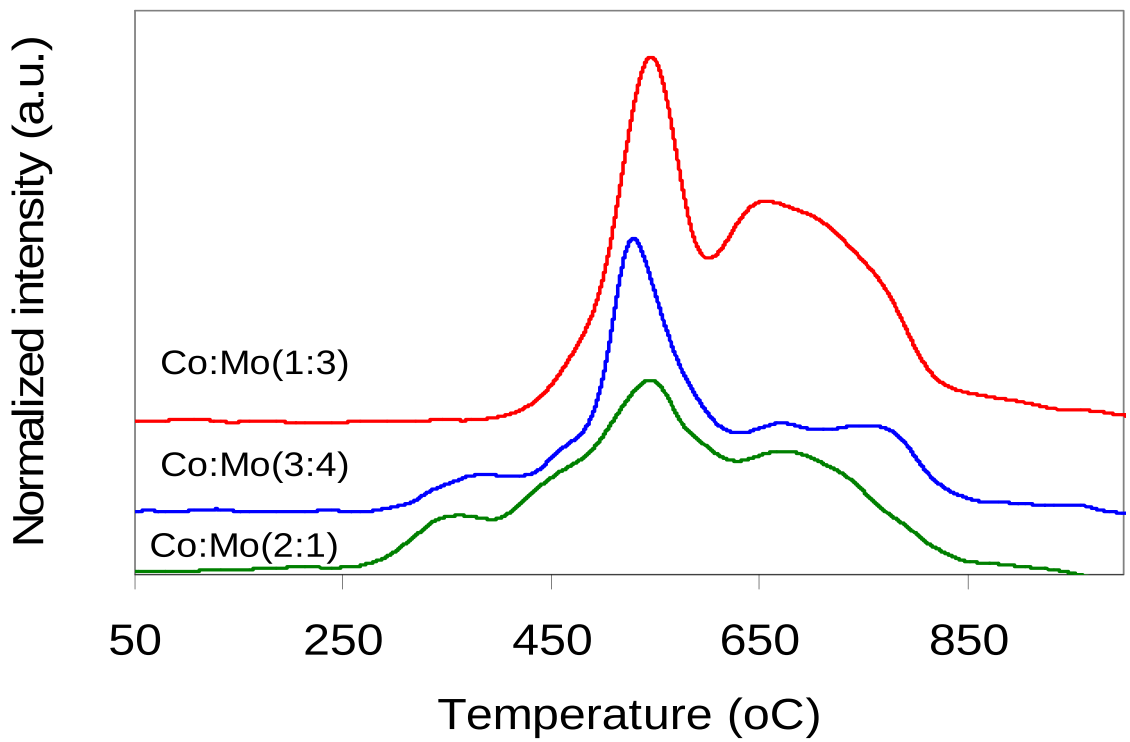


Characterization of the Catalysts After Calcination

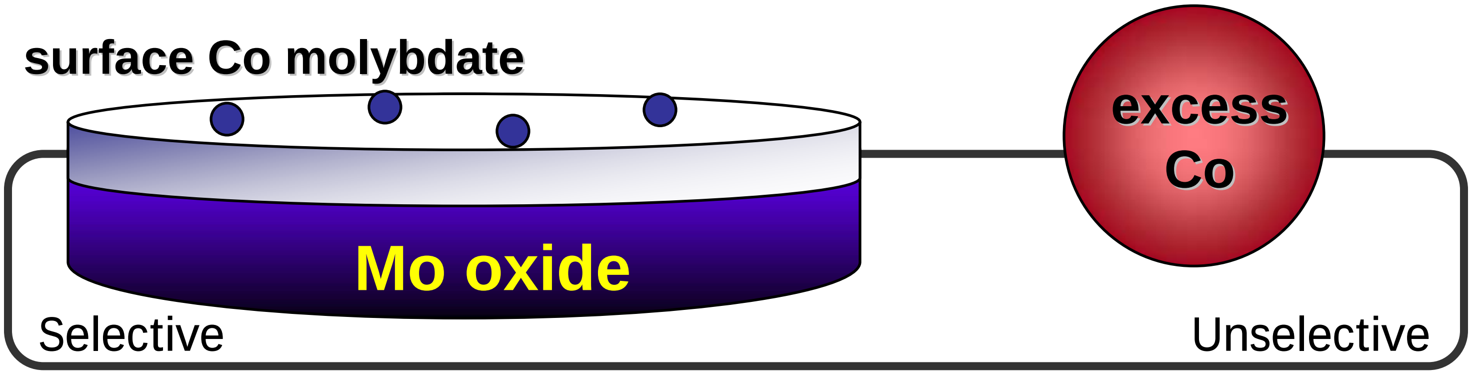


TPR

Stabilization by Mo inhibits reduction of Co

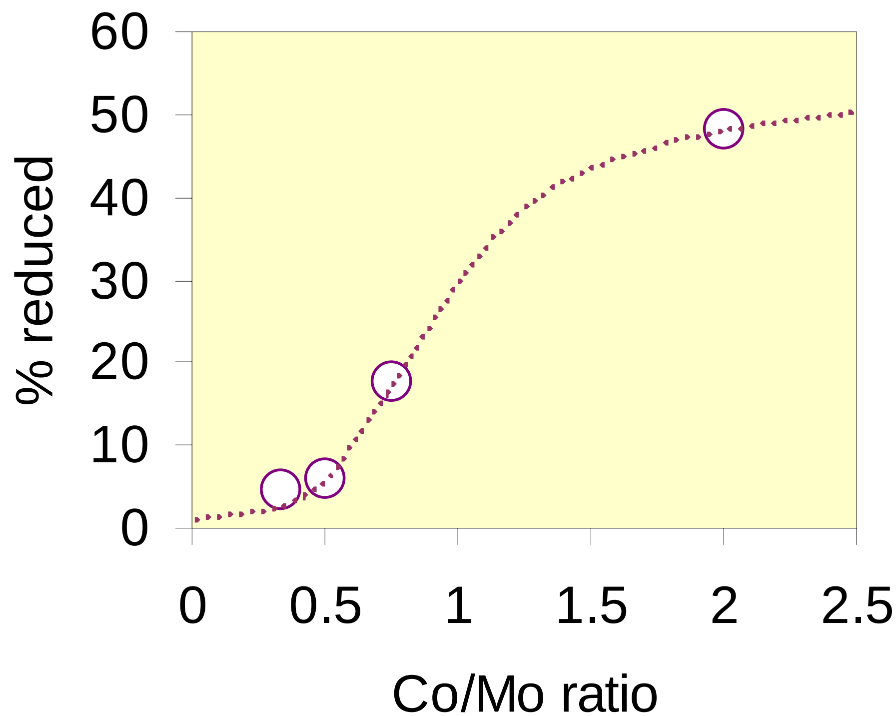


Characterization of the Catalysts After Reduction

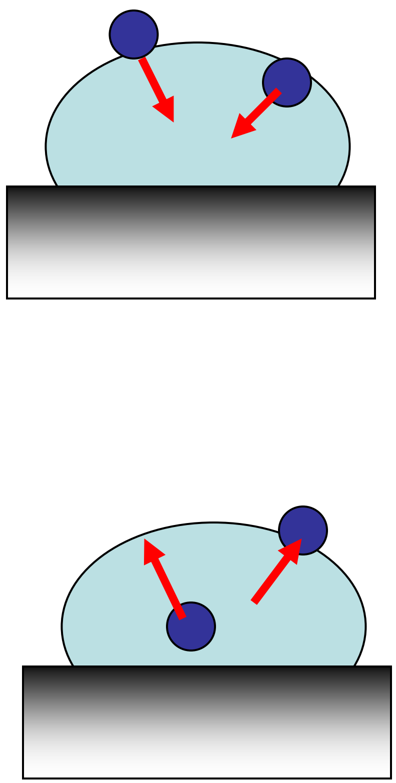


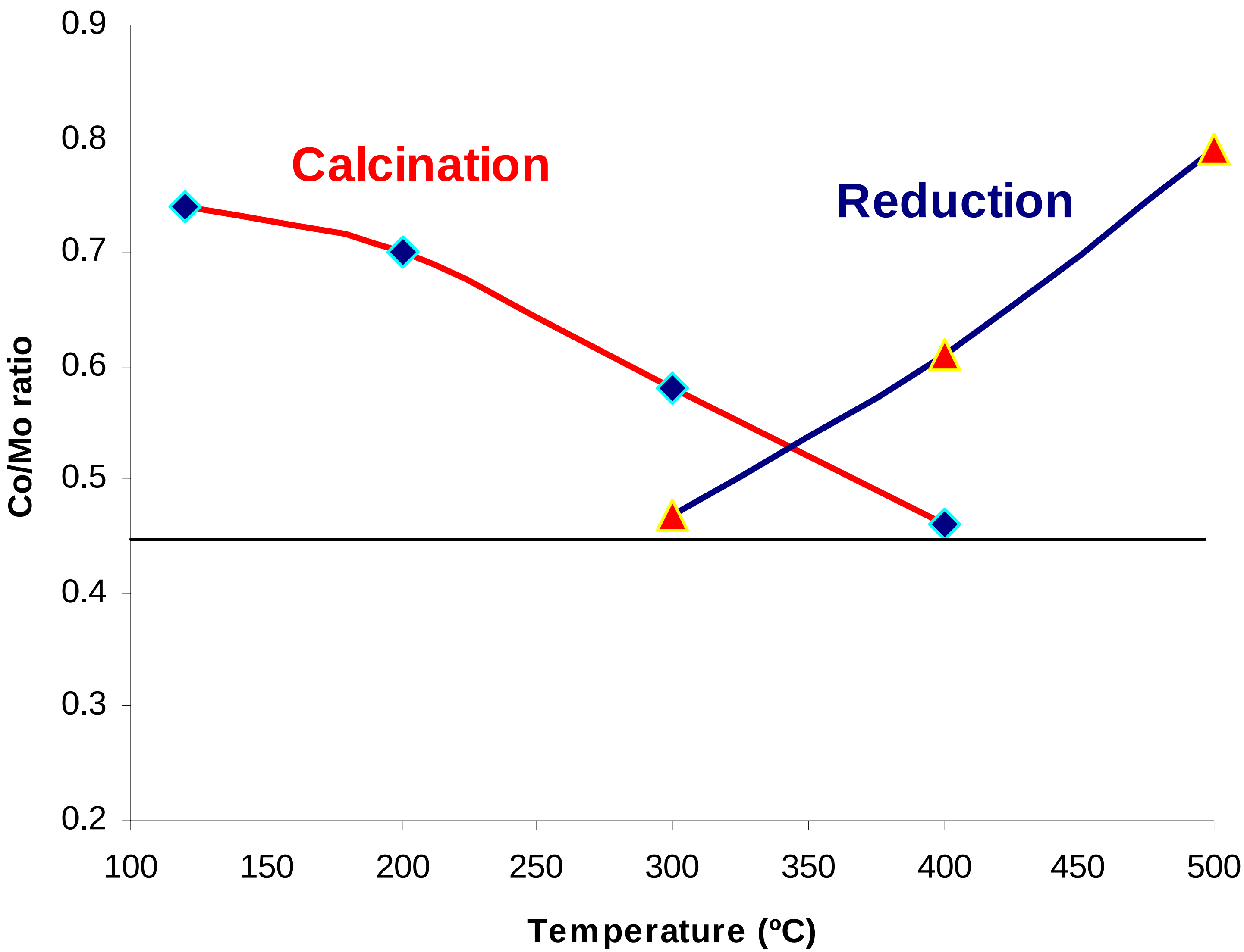
XPS

A much larger fraction of Co gets reduced as the Co/Mo ratio increases



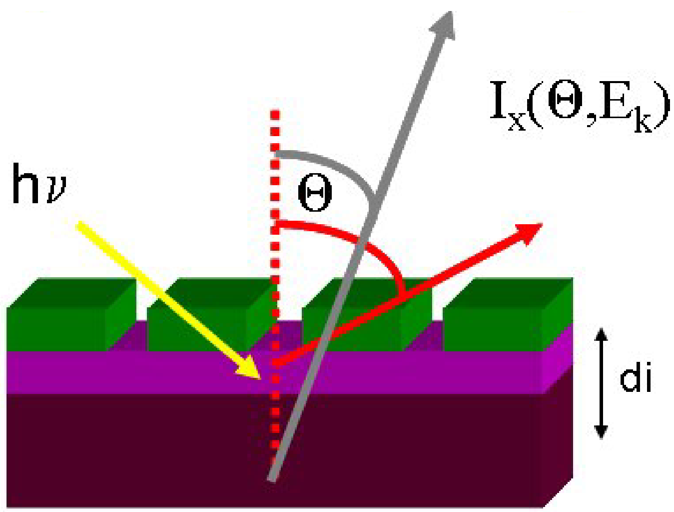
Surface Co/Mo ratio as measured by XPS



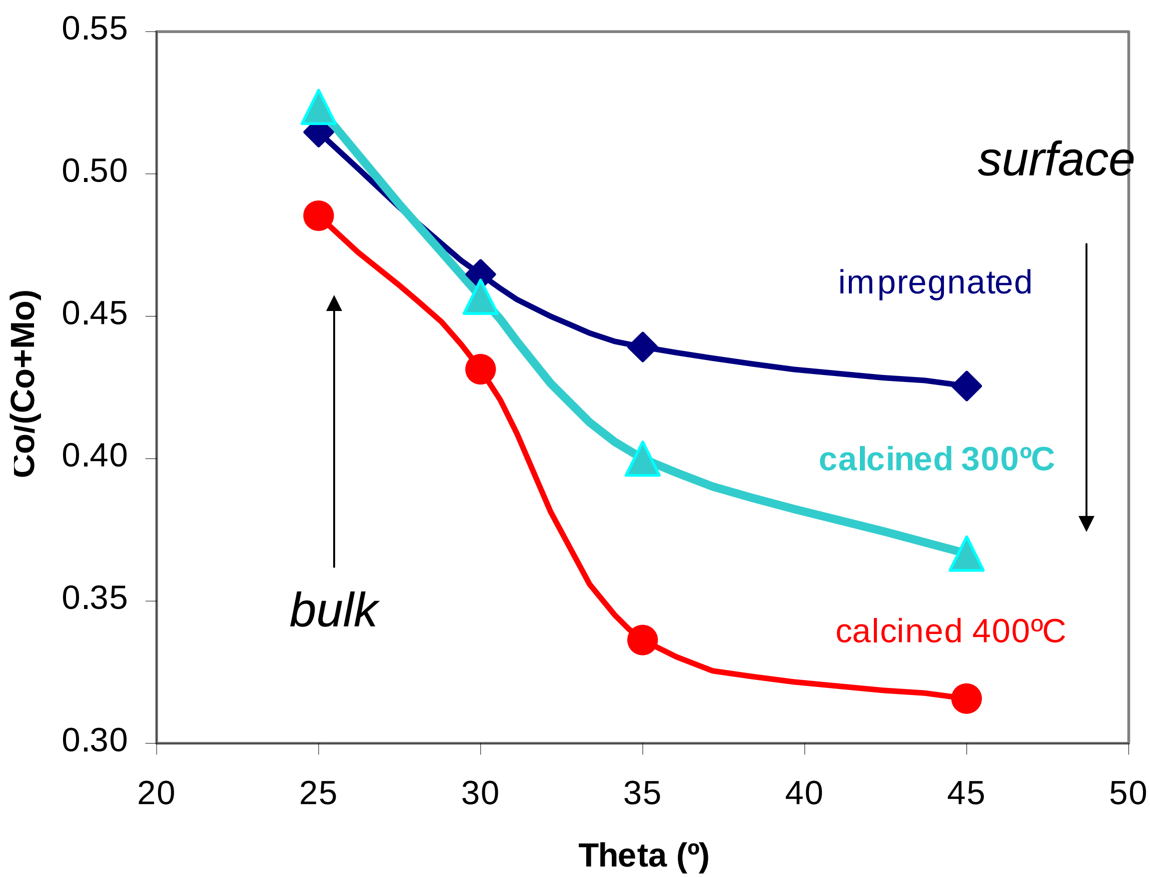


Angle-resolved XPS

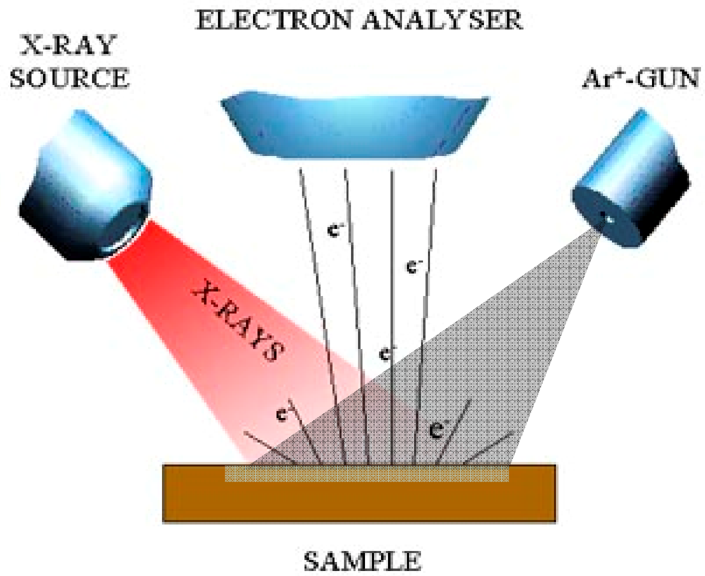
Co leaves the surface as the temperature of calcination increases



effective information depth di varies with polar angle θ

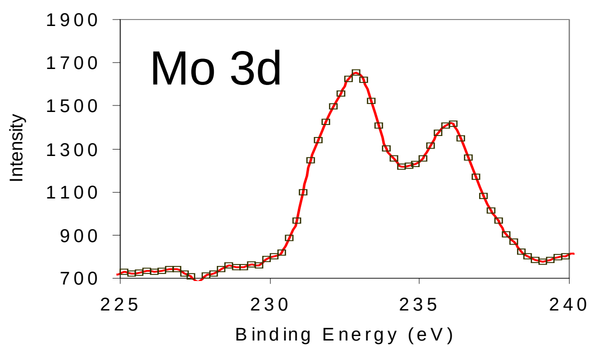


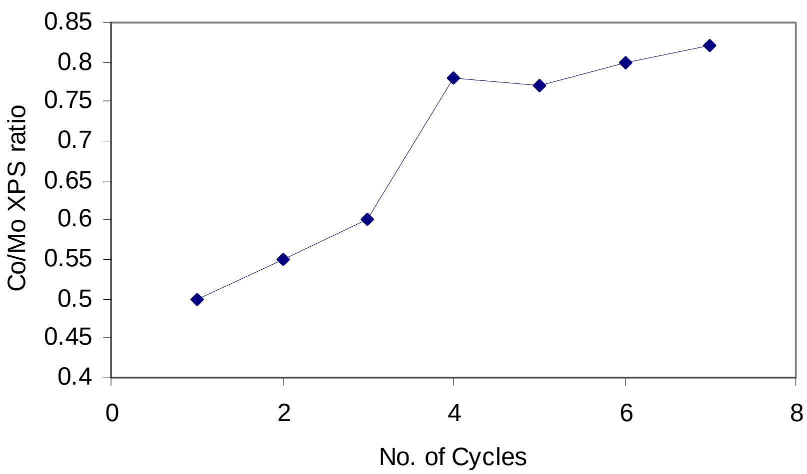
Sputter Depth Profiling



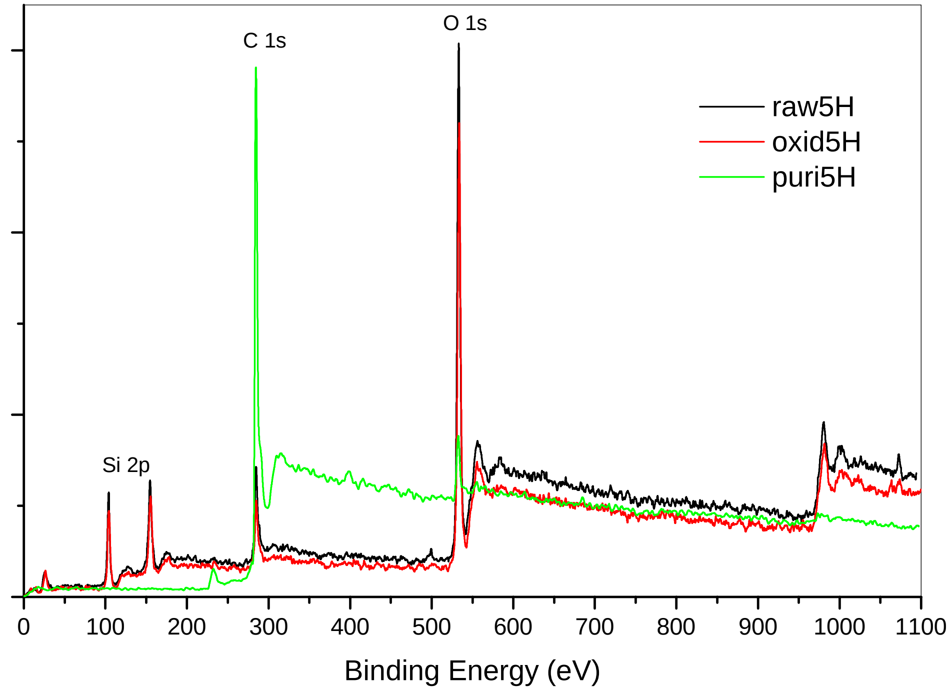
Typical Conditions

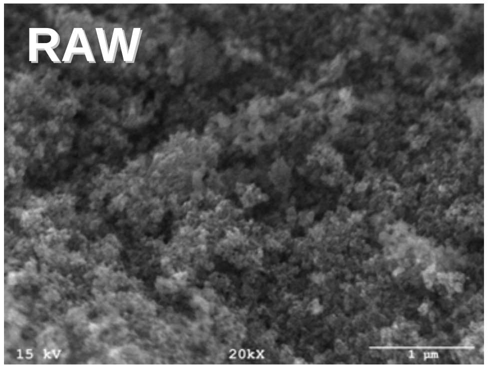
- Ion energy: 5 keV.
- 2 μA current intensity
- about 1.7.10-7 mbar pressure
- Ion gun emission current: 13.5 mA (90% of 15 mA)
- Ion incidence angle: 62°
- Sputtering time per cycle: 90 seconds

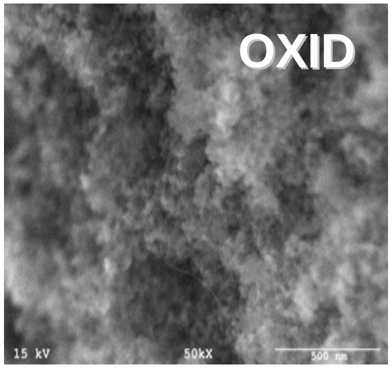


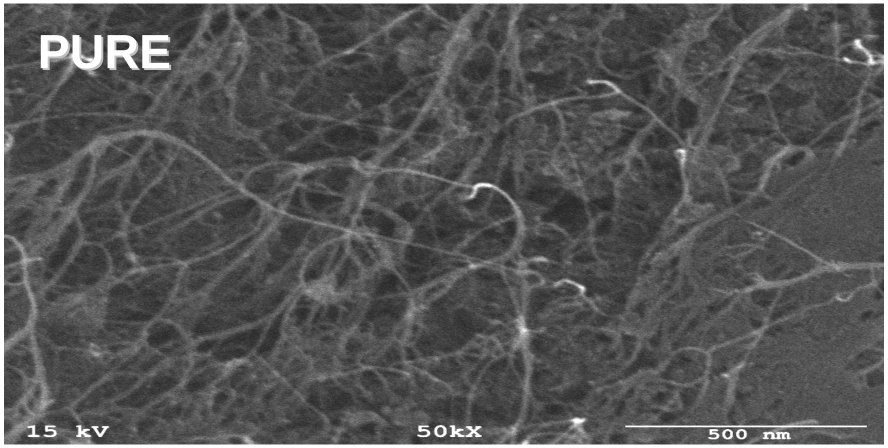


<u>Example 3</u>: Purification of Single-walled carbon nanotubes



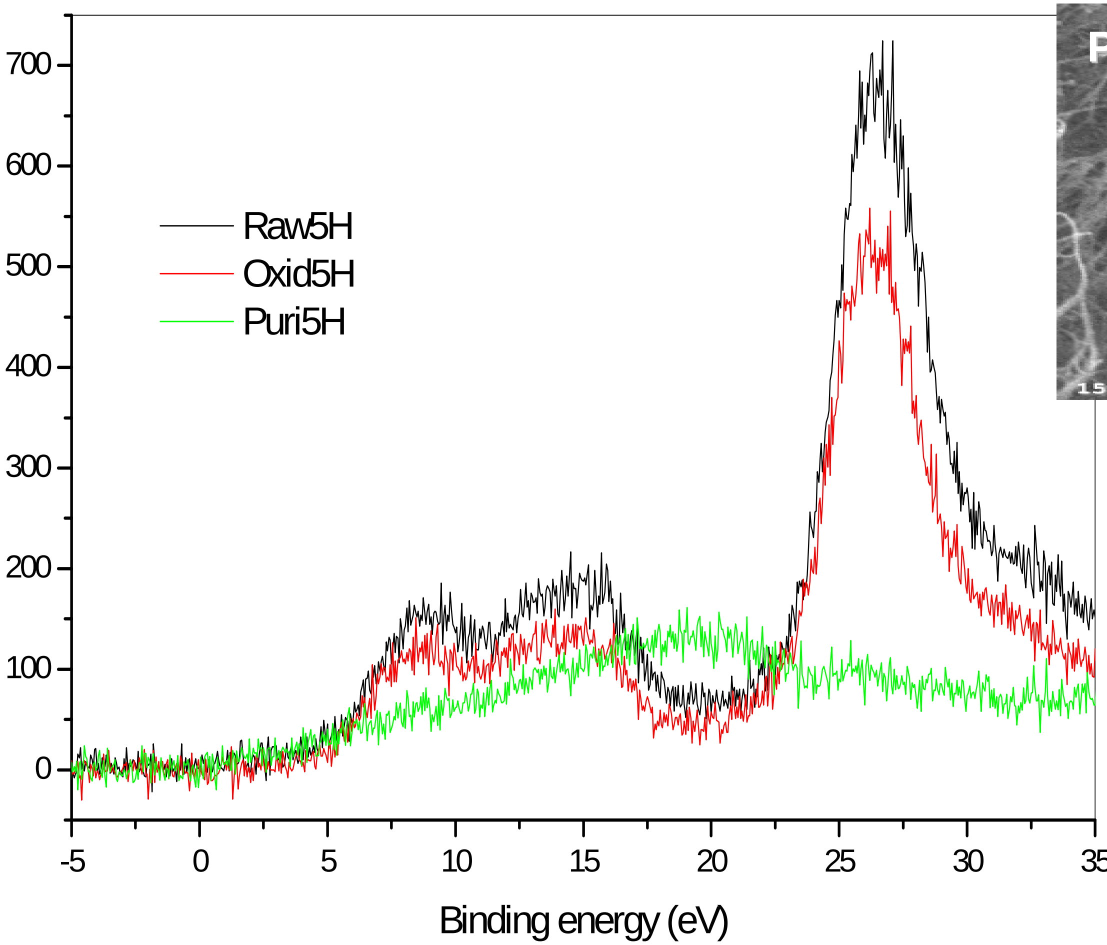


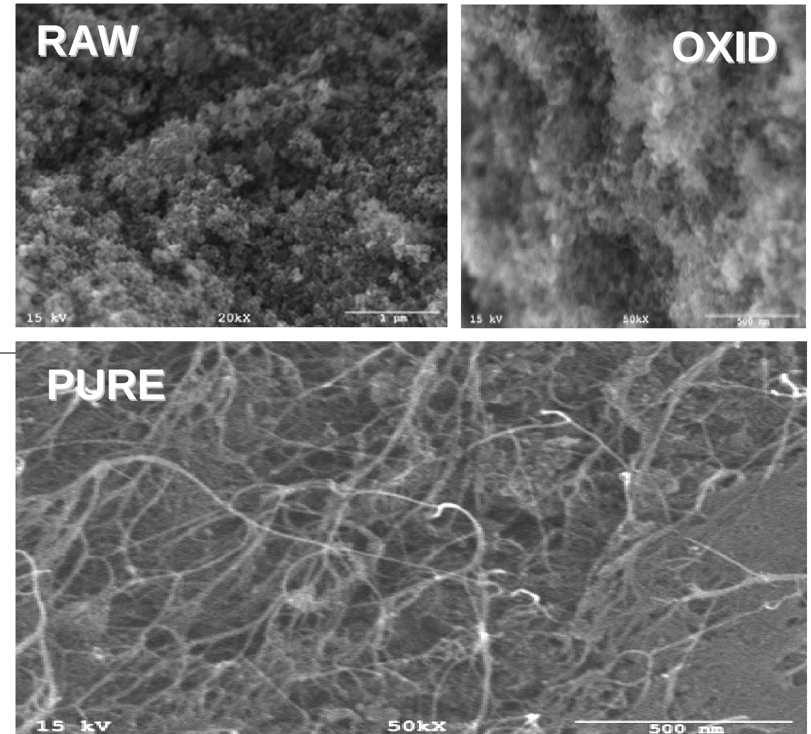




FileName	C1s	O1s	Na1s	Si2p	Cl2p	Co2p	Mo3d	F1s
RAW	28.56	49	0.74	21.44	0.15	0	0.12	-
OXID	25.51	51.01	0.65	22.66	0	0	0.17	-
PURE	95.25	4.36	0	0	0	0	0.34	0.05

XPS Valence band





X-Ray Photoelectron Spectroscopy (XPS) at the University of Oklahoma

- Widely used surface analysis technique
- Capabilities:
  - Two X-ray sources (monochromatic)
  - Argon sputtering profiles
  - Ex-situ treatments
- Projects supported:
  - Catalysis
  - Nanotubes
  - Fibers and textiles
  - Polymers
  - Environmental science
  - Electrochemistry
  - Fuel Cells
  - Metal alloys
  - Composites