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XPS for environmental analysis

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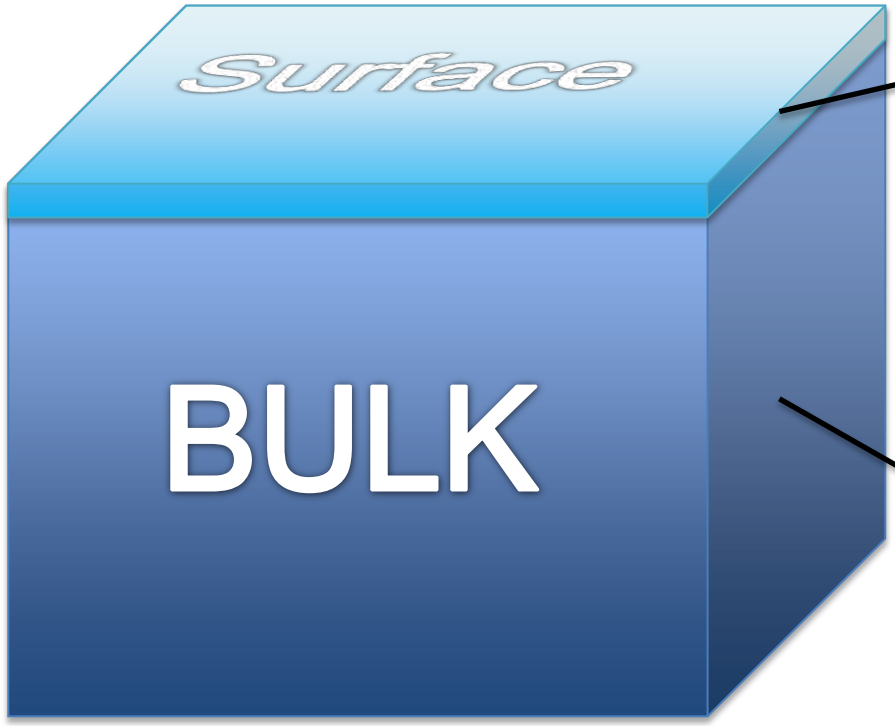
Materials Analysis

Bulk vs. Surface

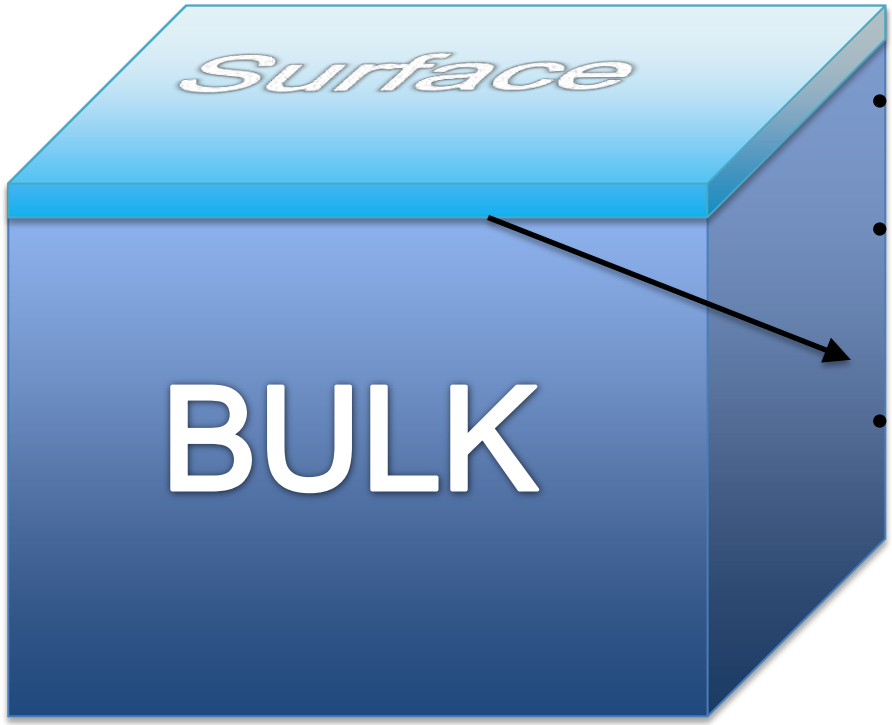


- Surface Composition
- Surface Roughness
- Homogeneity
- Surface charge
- Adhesion
- Surface reactivity

- Cohesion
- Density
- Morphologies
- Homogeneity
- Young's Modulus
- Hardness
- Composition

Surfaces & the environment

Surfaces important for many environmental areas



- Air pollution
  – surface chemistry toxicity
- Renewable energy
  - new materials Li battery PV
- Energy efficiency
  - Catalysts use surface reaction
- Environmentally preferable products
  - Research into alternatives materials such as Cr VI pre-treatments

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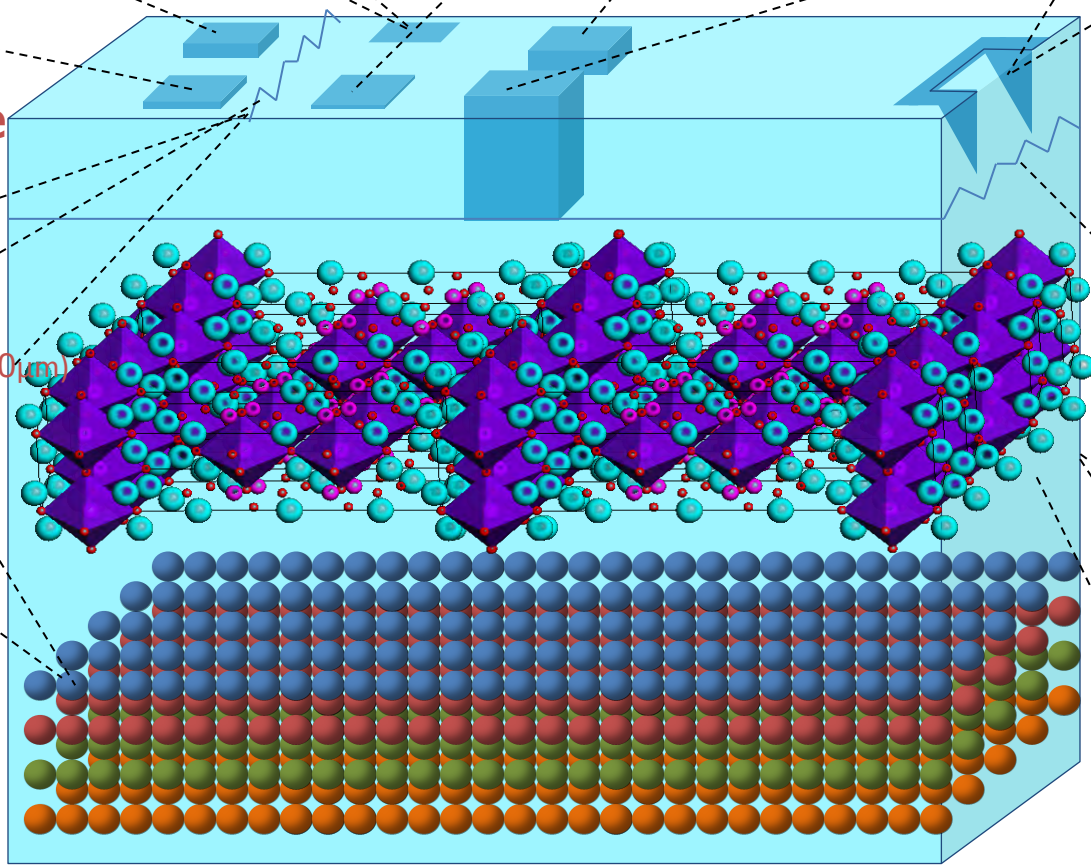
Bulk vs. Surface: Techniques



UHV ToF-SIMS (<1nm)

Surface

UHV ISS (top atomic layer)

UHV XPS (1-12nm)

UHV AES (1-5nm)

Sub-Surface

Raman (1-5µm)

ATR-IR (0.2-2µm)

SEM-EDX (0.3-3µm)

Depth Profiling →Etching

Mono – sources

Cluster Ions

10 nm

300 nm

Surface Profile

AFM (0.1nm-20µm)

STM (0.01 nm)

Interferometry (500µm)

Buried Layer

XRR (0.001-1µm)

900 nm

Atomic Scale

TEM-EDX (2-100nm)

TEM-EELS (2-100nm)

Bulk

FT-IR (0.5-2µm)

XRF (1-10µm)

XRD (10nm-10µm)

Physical Properties

Tensile Testing

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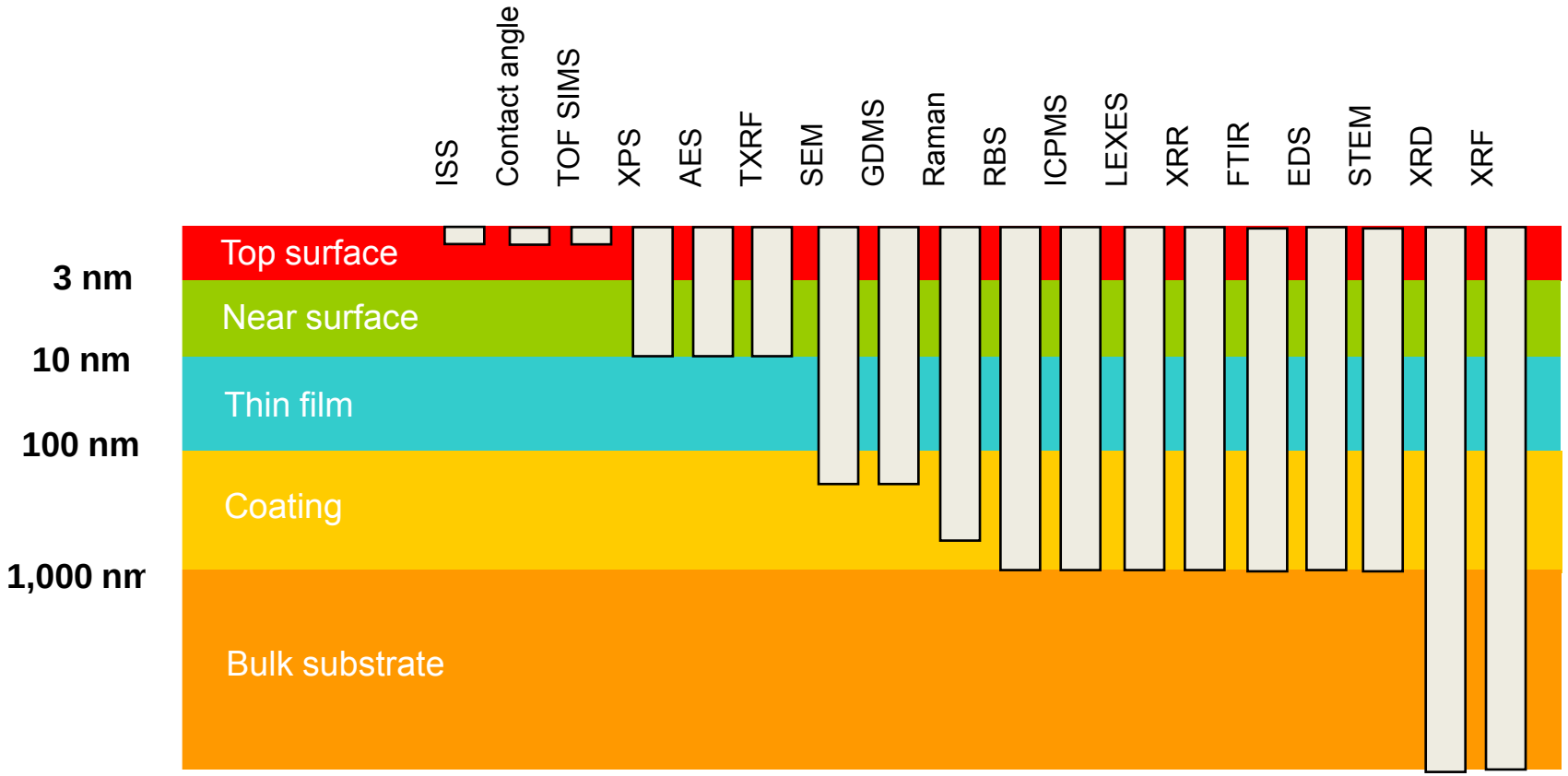
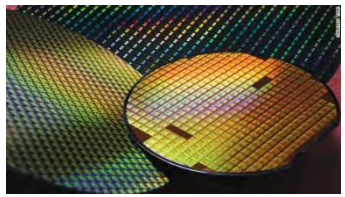
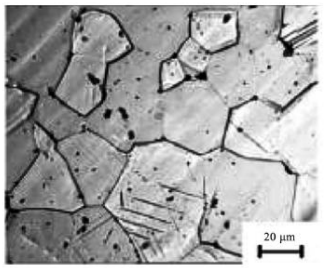
Typical Sampling Depths of Techniques

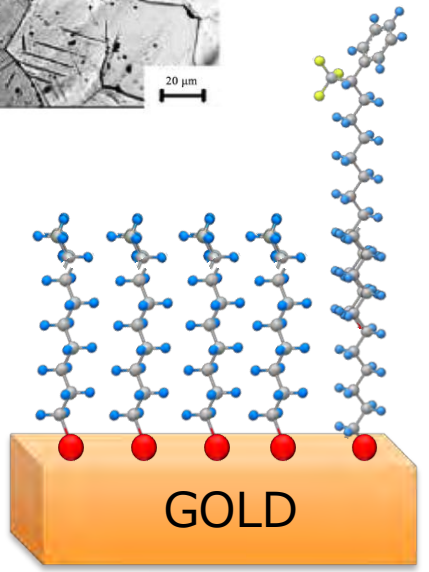


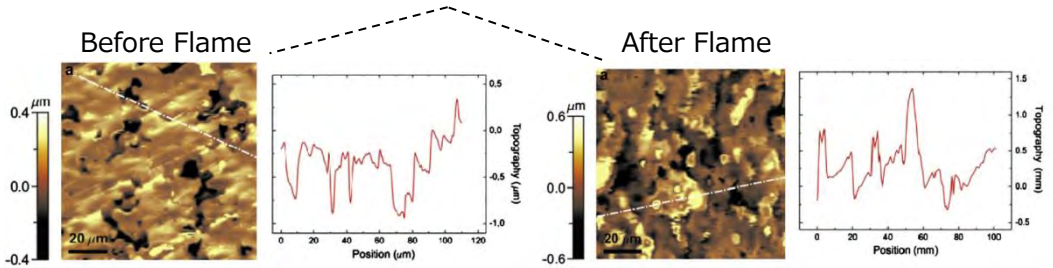
Surface Analysis: General use examples

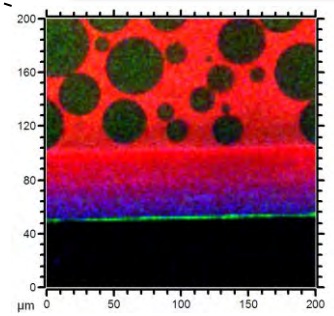
- Semi-conductors
- Bio technology
- Self assembled monolayers (SAMs)
- Thin films / coatings & adhesion
- Plasma / flame treated surfaces











Journal of Biomaterials and Nanobiotechnology, 2012, 3, 87-91
Polymer, 2010, 51, 3591-3605

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XPS's place in Surface Analytics

Features/ Advantages:

- **Quantitative** chemical analysis ~0.1 atom% detection limit
- Able to detect all **elements** except H and He
- **Non-destructive** analysis
- **Chemical state** information
- **Depth** profiling – accessing buried layers

XPS falls within HS 9022 19 classification

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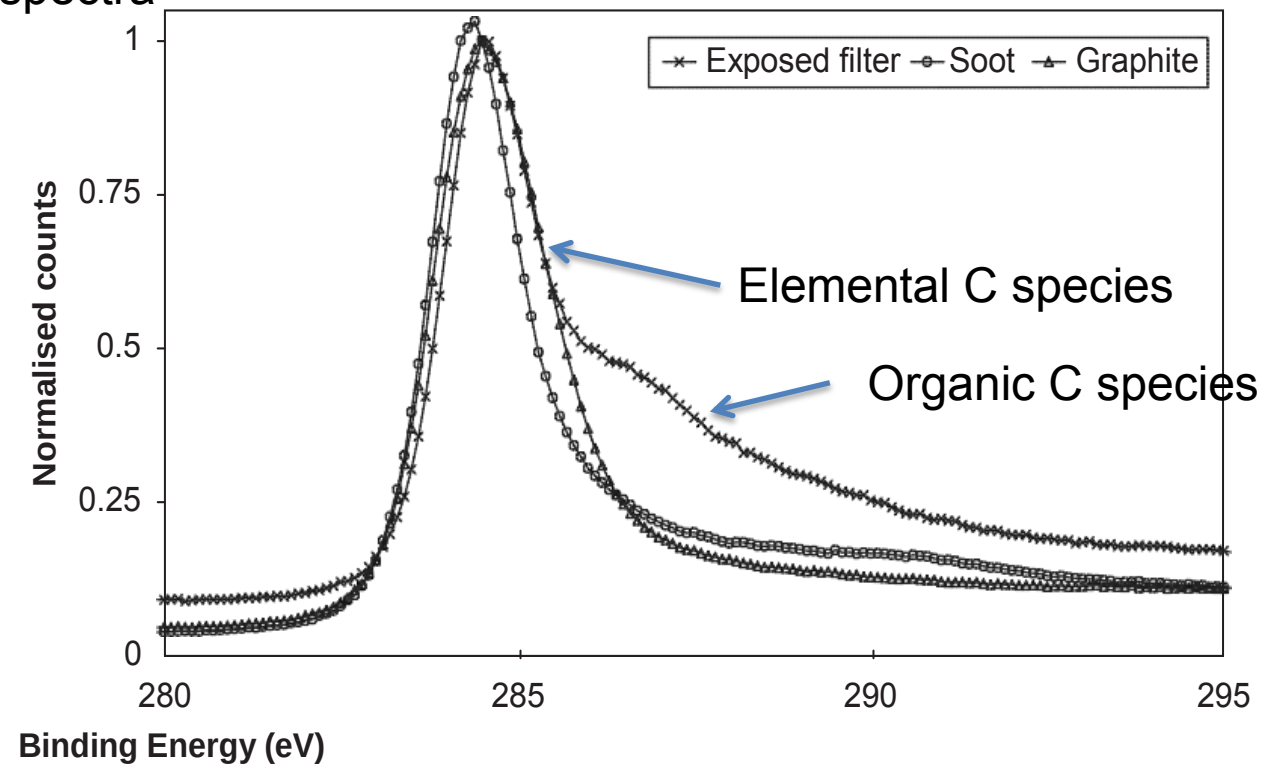
1. Air pollution control: Particulate analysis

- Composition of carbonaceous particles is of interest
- Carbon speciation data can provide information on source apportionment
- Surface specific data can also inform of the toxicity of particulates
- Example of analysis of particles collected at London roadside
  - Objective to compare elemental carbon composition with organic carbon composition

1. Air pollution control: Particulate analysis

C1s XPS spectra



Reference: RJJ Gilham *et al* Atmospheric Environment 42 (2008) p 3888-3891

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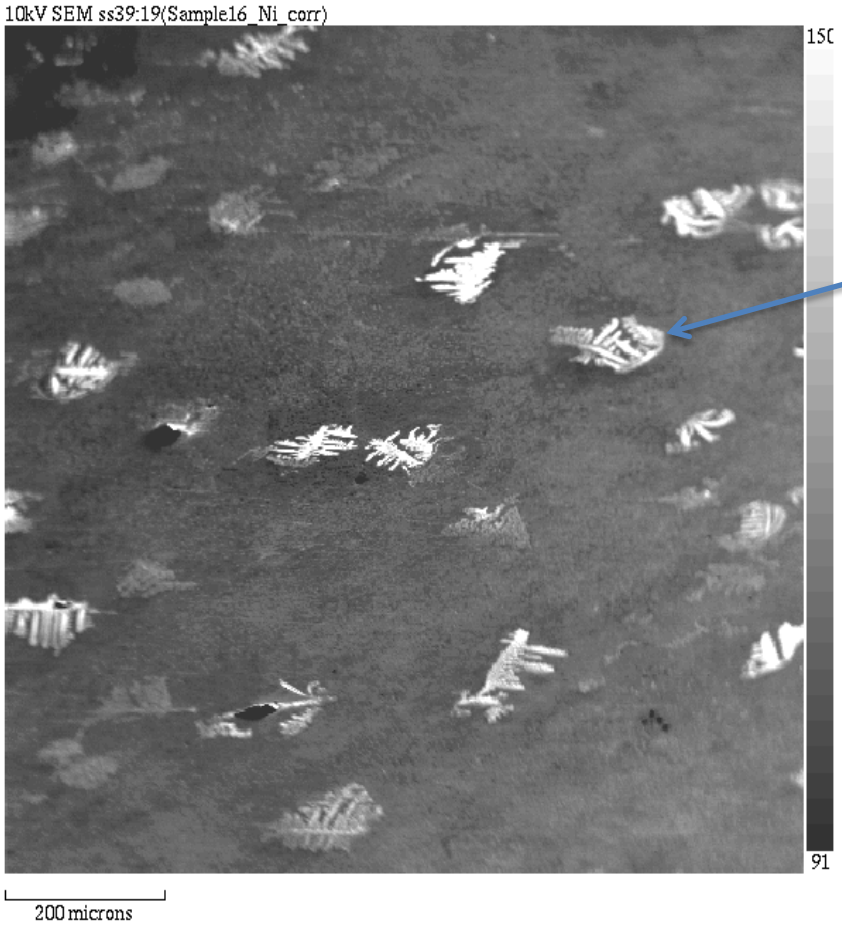
8. Environmental monitoring and assessment

- Ni test coupons exposed to standard outdoor weather in controlled experiment in Stockholm
- Objective to identify corrosion initiators
- Dendritic corrosion observed and analysed by XPS and related technique of Auger electron spectroscopy
  - S identified as the initiator of dendritic Ni oxide formation

8. Environmental monitoring and assessment

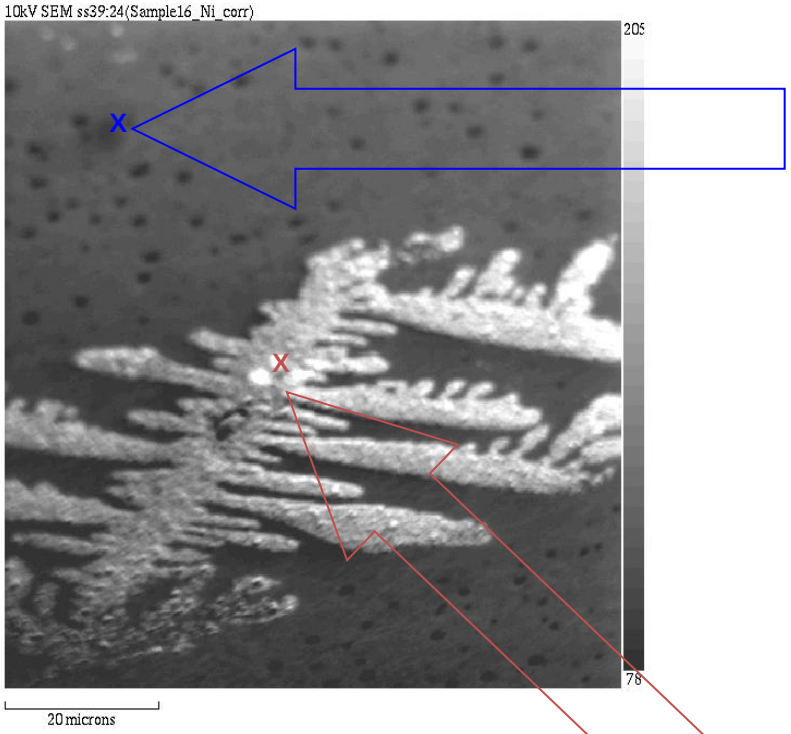


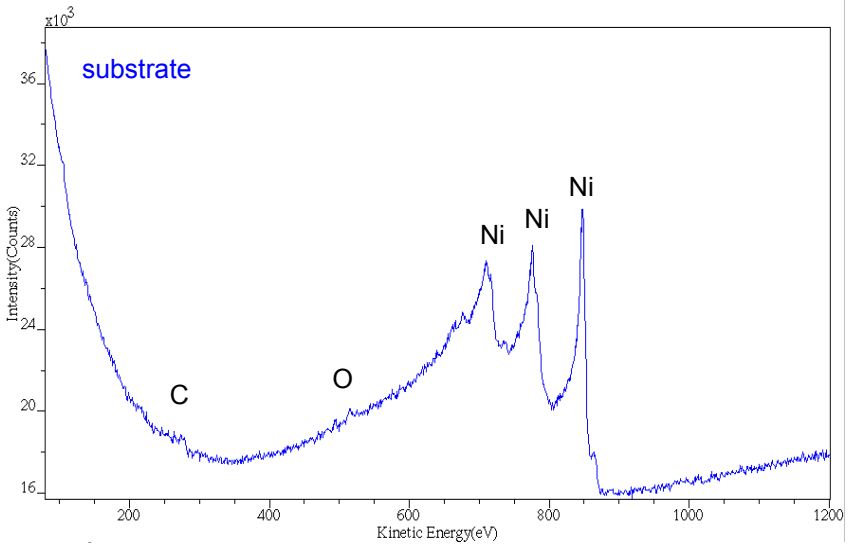
Dendritic corrosion observed by SEM

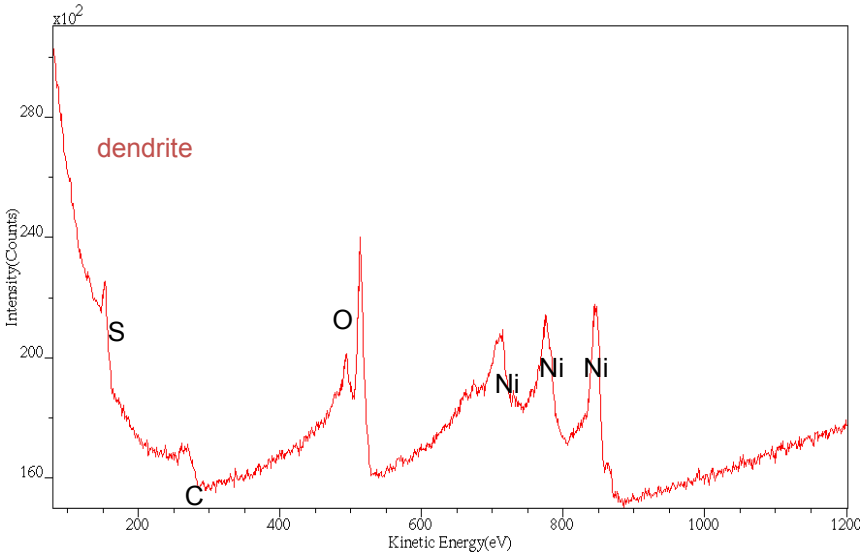
- material analysis by Auger electron spectroscopy

Reference:I.Odnevall & C. Leygraf J.Electrochem. Soc., vol 144, No. 10, October 1997, 3518-3525

8. Environmental monitoring and assessment



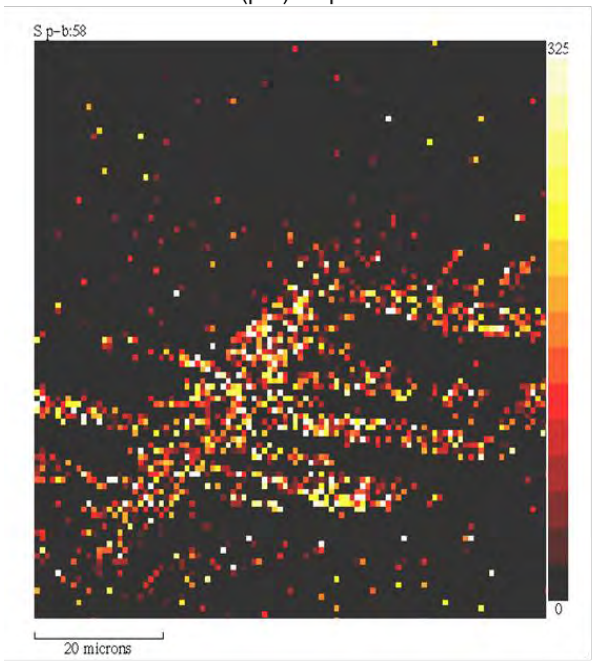




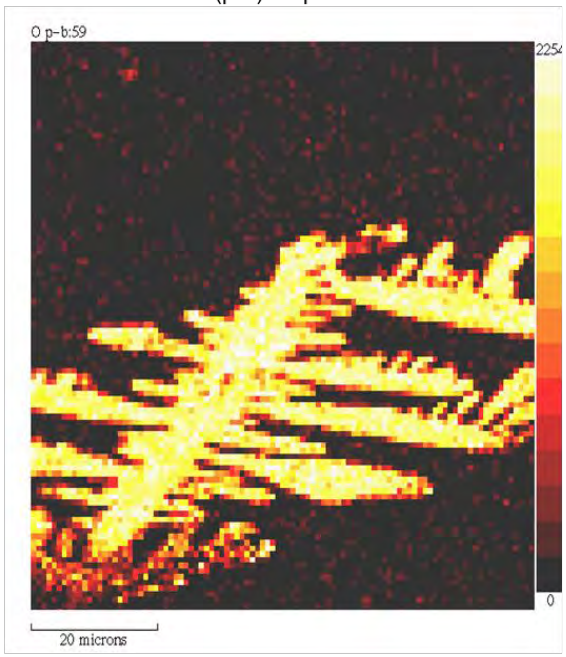
AES spectra show the presence of sulfur in corrosion product S < 1nm thick!!

8. Environmental monitoring & assessment

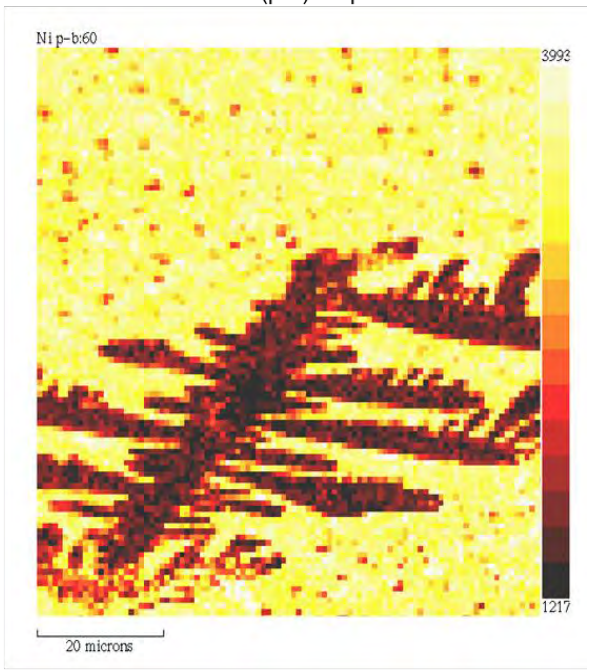
S (p-b) map



O (p-b) map



Ni (p-b) map

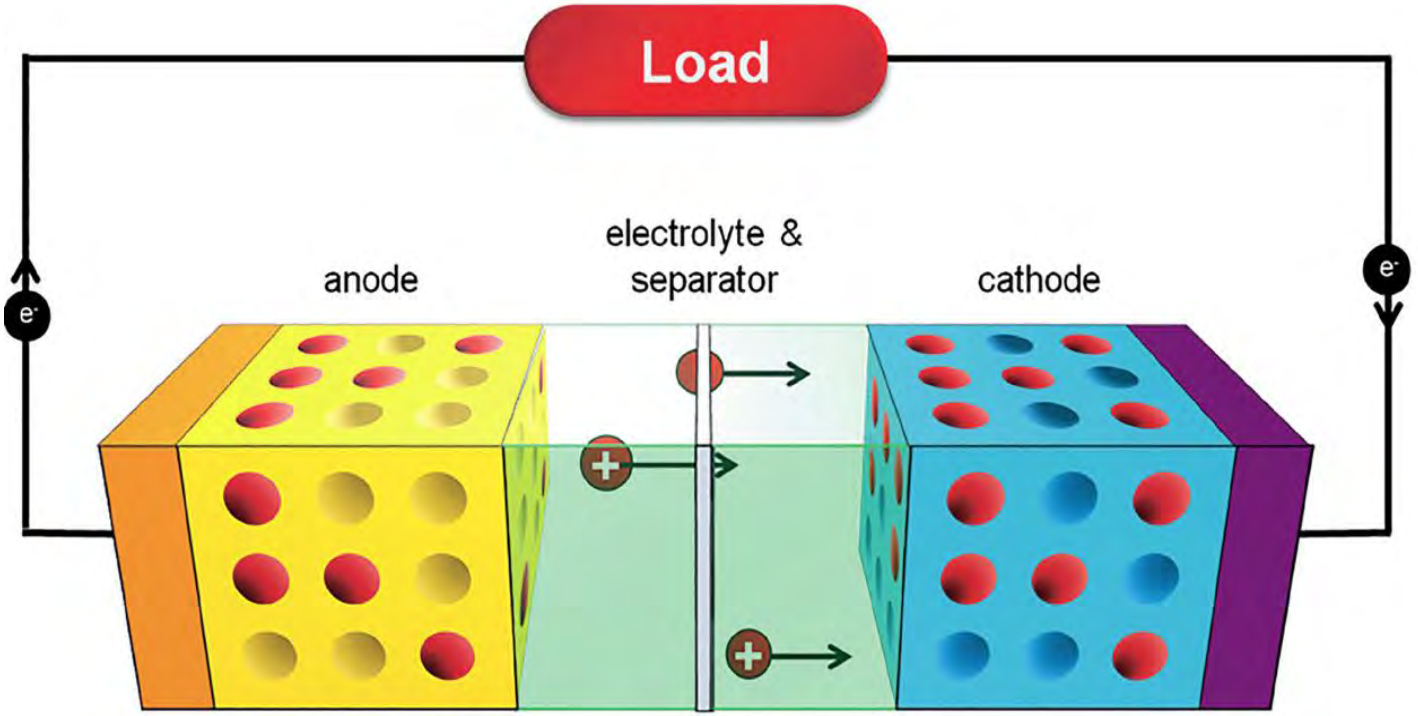


The images shown are peak - background maps.

Sulfur is unambiguously identified as the corrosion initiator but only present as a few atomic layers

6. Cleaner and renewable energy

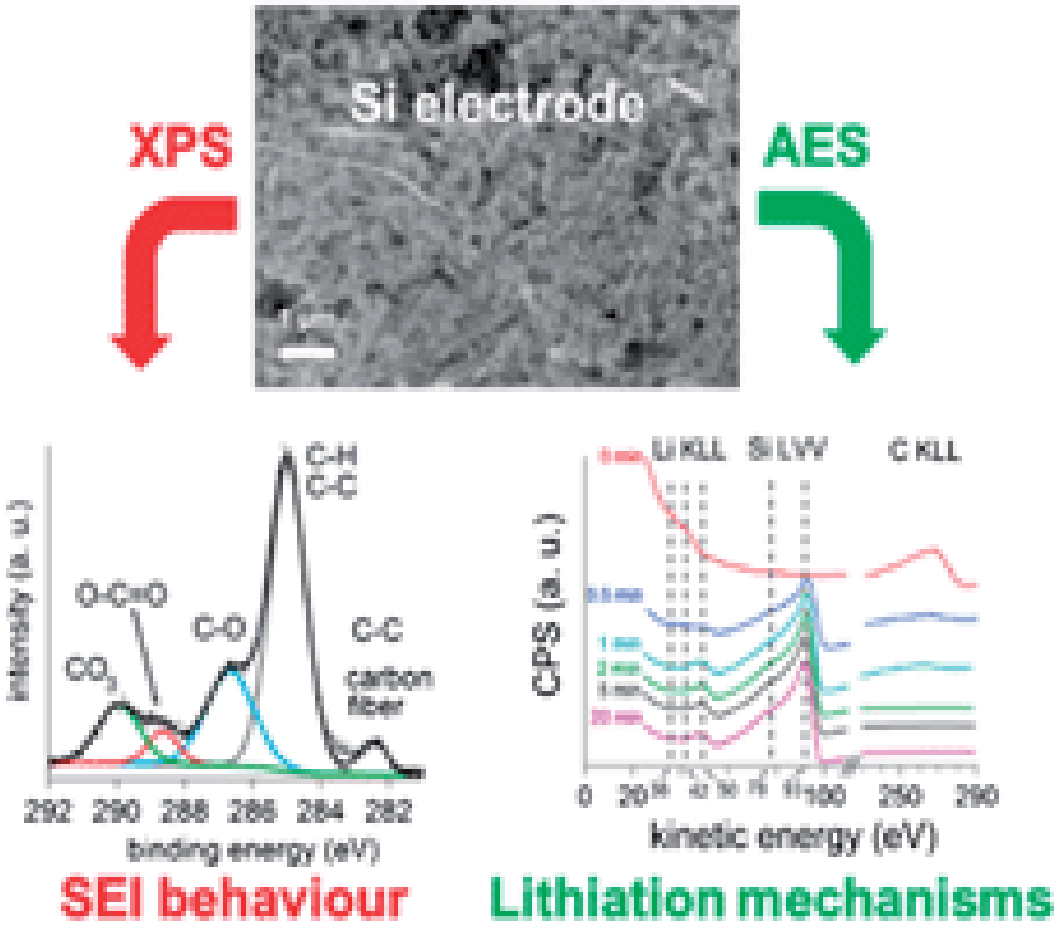
Operates via transfer of charge in form of Li^+ ions and recharged by reverse process



One problem with the lifetime is the formation of a barrier at the interface or solid electrolyte interphase SEI

6. Cleaner and renewable energy

J. Anal. At. Spectrom., 2014,**29**, 1120-1131



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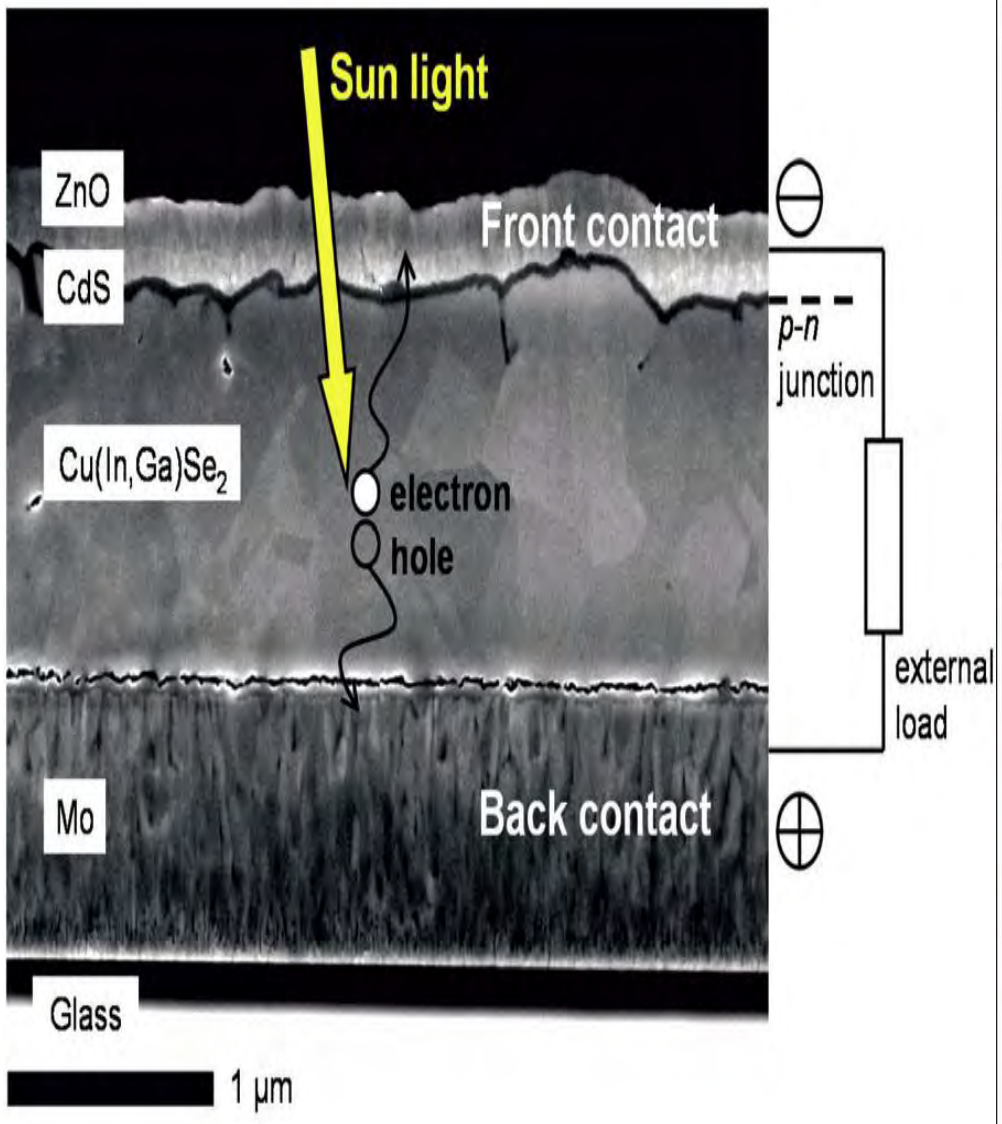
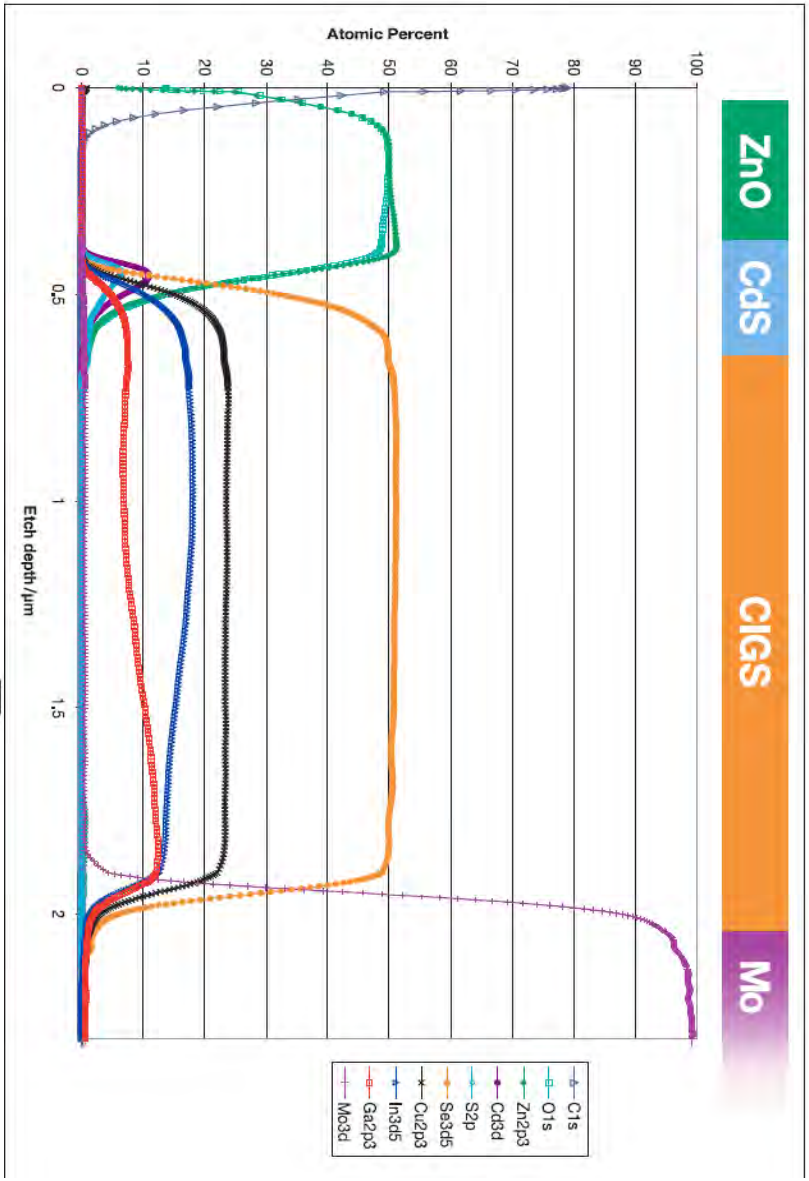
6. Cleaner and renewable energy





6. Cleaner and renewable energy

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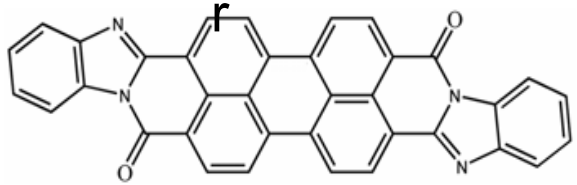

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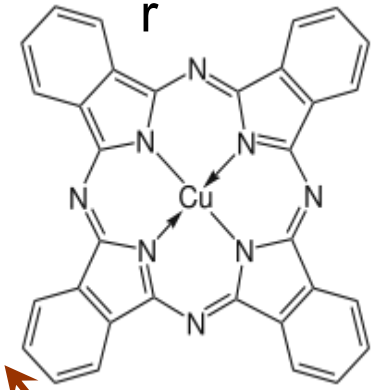

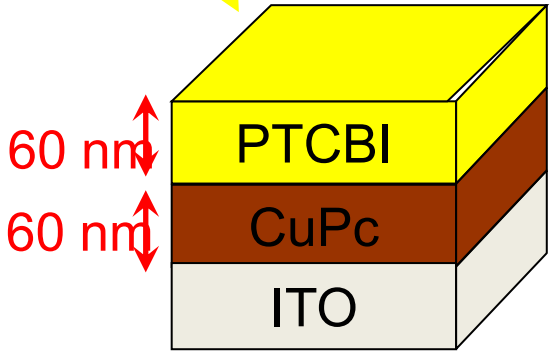

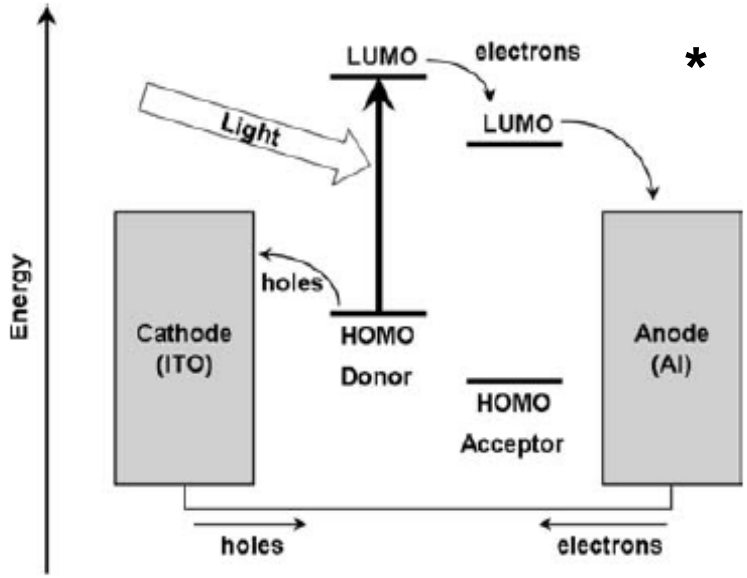

Benanti *et al. Photosyn. Res.*, **87**, 73, 2006

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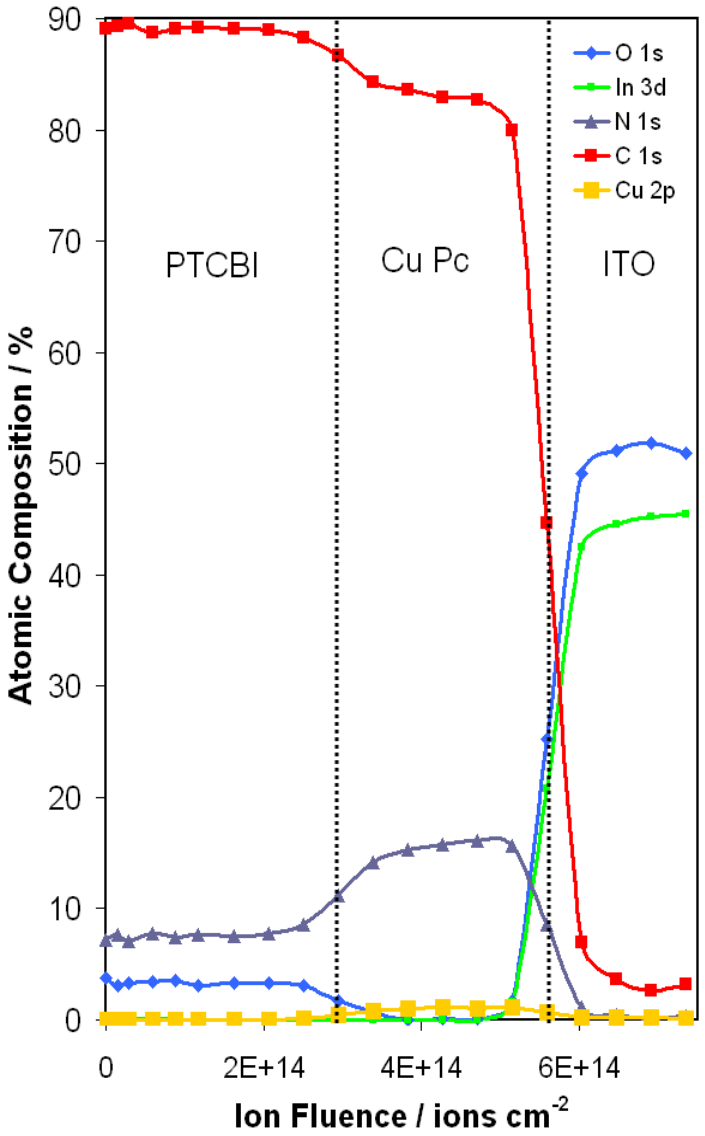
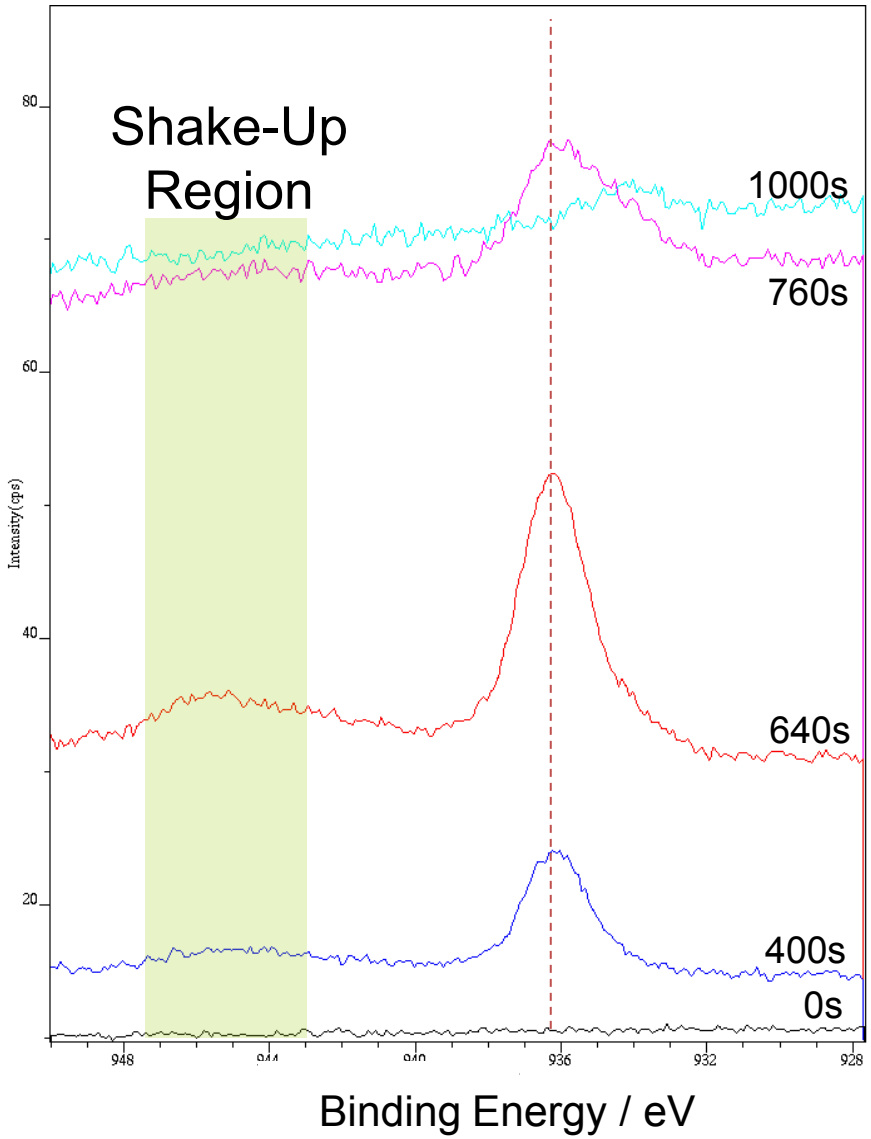
6. Cleaner and renewable energy





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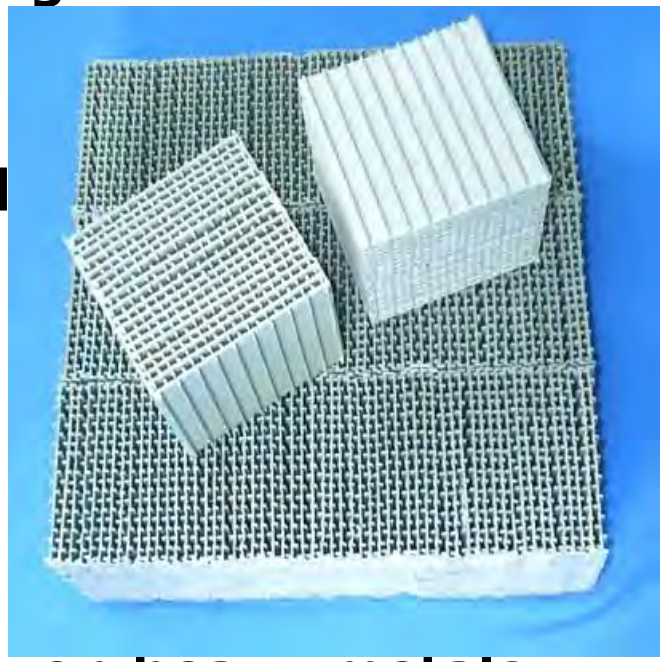
9. Resource efficiency

- Catalysts used in many environmental applications ranging from reducing CO_2 emissions in vehicles to improving efficiency of industrial processes
- Catalysts work as they have a very high surface area compared to bulk area



- Very high surface area silicon based 10nm nano-particles used to support CeO_2 catalyts

- Reducing gases applied to catalyst
- Studied by XPS for optimisation
- Si nano-particles reduce dependency on heavy metals

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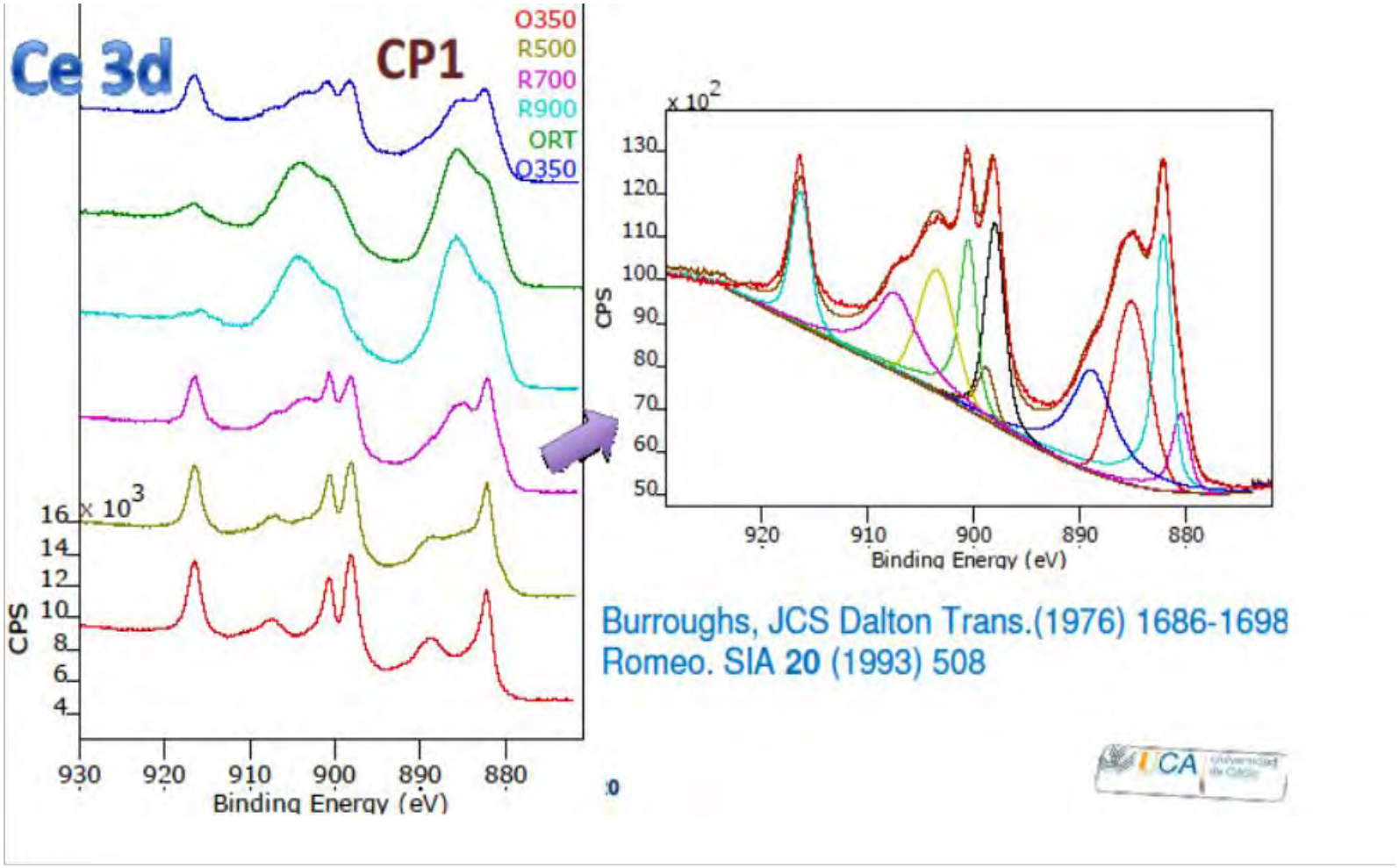
9. Resource efficiency



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Wrap-up, conclusions

- XPS and other surface analysis techniques have a general use
- This technique is an enabler in new materials or nano-technologies, essential for environmental applications the tarif associated with 9022 classification restricts access to this technology
- Market for XPS is global, Chinese Academy of Science to USA Department of Energy
  - University research laboratories
  - National laboratories or research groups MPI, RAS, CAS, CNRS
  - Large corporate research centres Shell, 3M, Samsung