Scientific Innovation Through Integration

EMSL

National Nanotechnology Initiative Workshop

Nanomaterials and the Environment & Instrumentation, Metrology, and Analytical Methods

October 6-7, 2009, Arlington, Virginia

Panel 9
Development of Standards for nanomaterials properties

Develop methods to characterize a nanomaterial's spatio-chemical composition, purity, and heterogeneity

Story Lines

- Conduct research on reactive metal nanoparticles (US DOE research program on **Fe metal-core oxide-shell** particles – demonstrate importance of sample history and time on NP behavior)
- Nanoparticle characterization challenges in our DOE user facility, EMSL (Environmental Molecular Sciences Research Lab)
  - General issues – **time, history, handling**
  - Role of **surface analysis methods** including information that can be extracted from XPS (beyond what is normally done)
  - Importance of **new instrumentation** used in "advanced" ways
- Standard and guide activities related to ASTM E42 on surface analysis and ISO TC201 on surface chemical analysis
  - Technical report from TC201 linked to needs of ISO TC 229 on nanotechnology
  - ASTM E42 analysis protocols

Nanoparticles are not created equal

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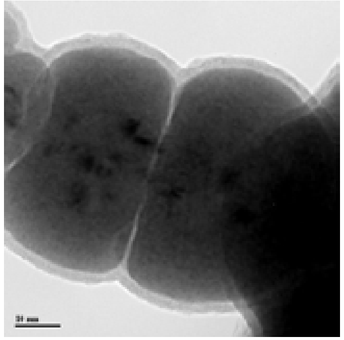
Toxic Breakdown Products

$$CCl_4\ (CT) \xrightarrow[-1\ Cl^-]{+1\ e^-} \bullet CCl_3 \xrightarrow{+\bullet H} HCCl_3\ (CF)$$

$$\bullet CCl_3 \xrightarrow[-1\ Cl^-]{+1\ e^-} :CCl_2 \rightarrow HCOOH,\ CO,\ etc.$$

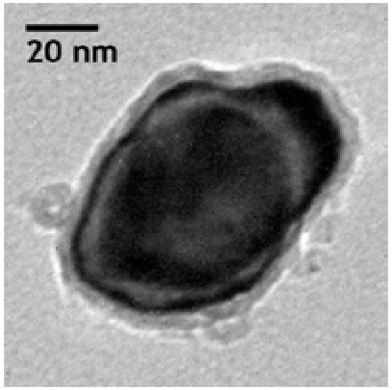
Benign Breakdown Products

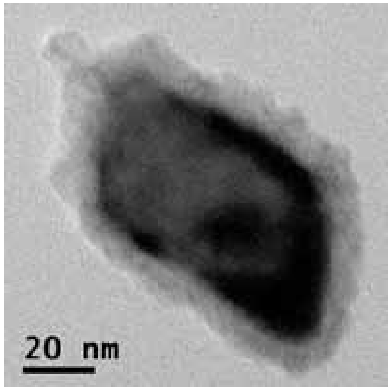


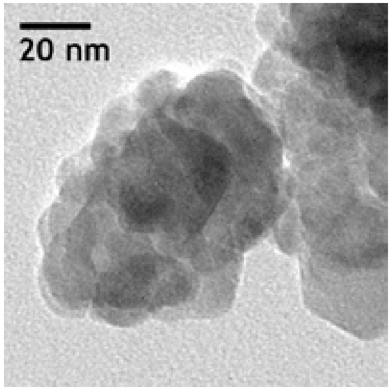
Particles change with time in solution

Particles formed by reduction in hydrogen exposed to pure water

0 day **1 day** **5 day**







Initially continuous dense oxide shell becomes less dense and other oxide nano-structures form

Shell changes and more oxide forms

Sarathy et al. (2008) J. Phys. Chem. C

Reactivity varies as particles change (Batch interaction with CCl_4)

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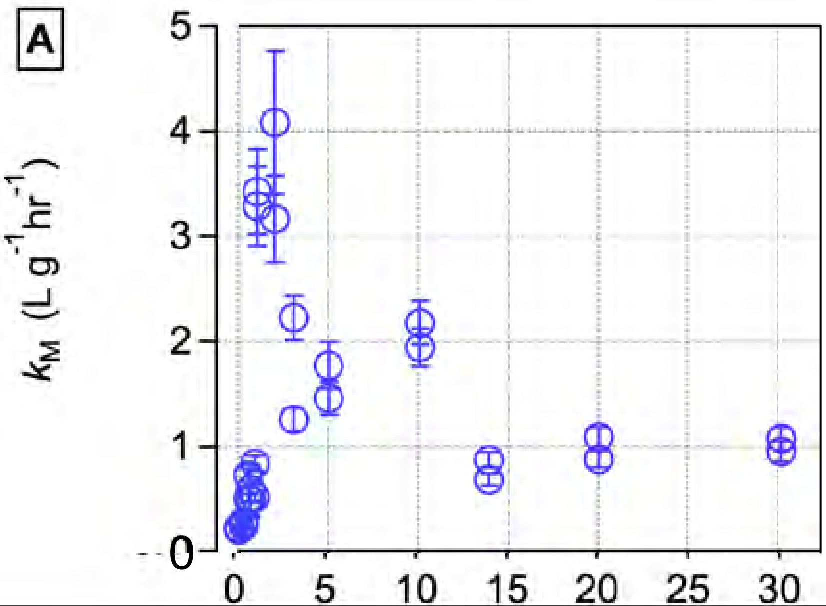
Reaction Rate



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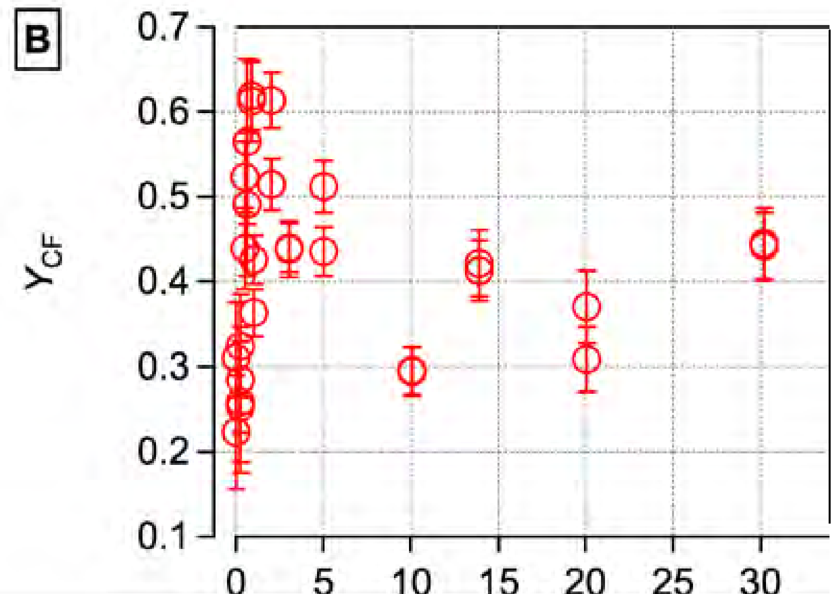
CF Yield



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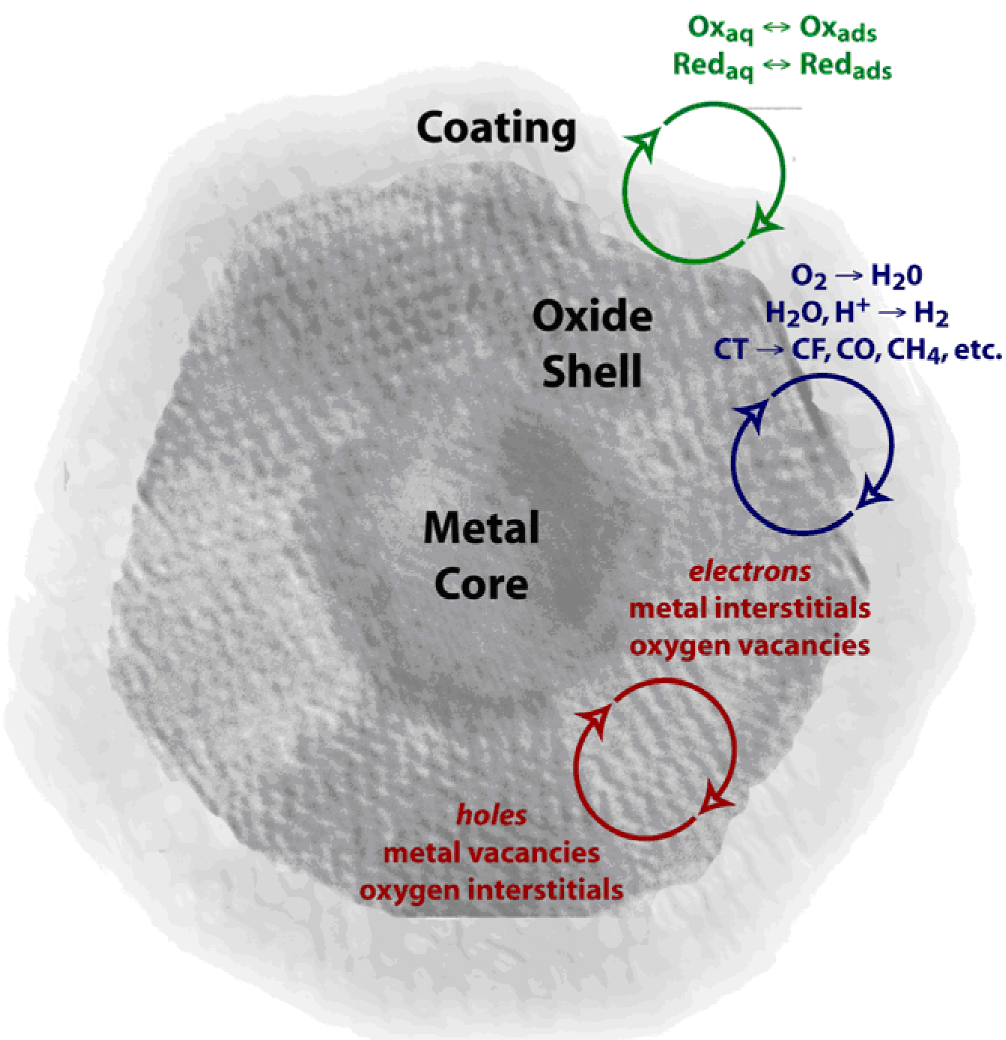
Sarathy et al. (2008) J. Phys. Chem. C

Behavior of nanoparticles depends on particle structure and history



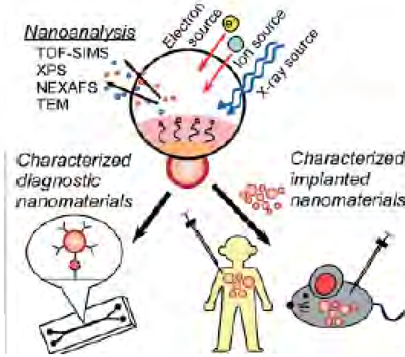
Nanoparticles in solution make up a dynamic, highly reactive system.

Different types of interactions occur at specific locations:

- **Surface sorption**
- **Interaction with water and contaminants, altering shell composition, chemistry and structure**
- **Charge and mass transport in shell**
- **Iron Oxidation**

DOI: 10.1002/adma.200701760

Nanobiomaterials and Nanoanalysis: Opportunities for Improving the Science to Benefit Biomedical Technologies**



By *David W. Grainger** and *David G. Castner*

*Nanomaterials advocated for biomedical applications **must exhibit well-controlled surface properties** to achieve optimum performance in complex biological or physiological fluids. Dispersed materials with extremely high specific surface areas **require as extensive characterization** as their macroscale biomaterials analogues. However, current literature is replete with many examples of nanophase materials, most notably nanoparticles, with **little emphasis placed on reporting rigorous surface analysis or characterization**, or informal implementation of surface property standards needed to validate structure-property relationships for biomedical applications. Correlations of nanophase surface properties with their stability, toxicity and biodistributions are essential for **in vivo** applications. **Surface contamination** is likely, given their processing conditions and interfacial energies.*

SMALLTIMES

Particle size matters: Studies fail to include basics for assessing toxicity

By Candace Stuart - March 17, 2006

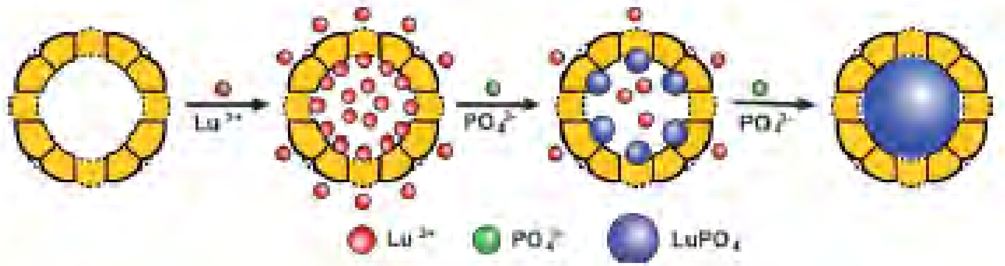
Vicki Colvin (Rice University) has a question for colleagues who study nanoparticles and how they may affect people and the environment. **"Exactly what do you mean by size?“**

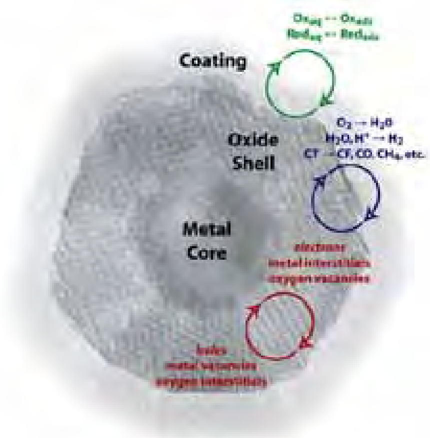
When chemists, toxicologists or other researchers report the dimensions of an engineered nanoparticle, are they measuring the **core**, the **core plus a coating**, or perhaps the **core**, a **coating** and **attachments** that help nanoparticles adhere to cells?

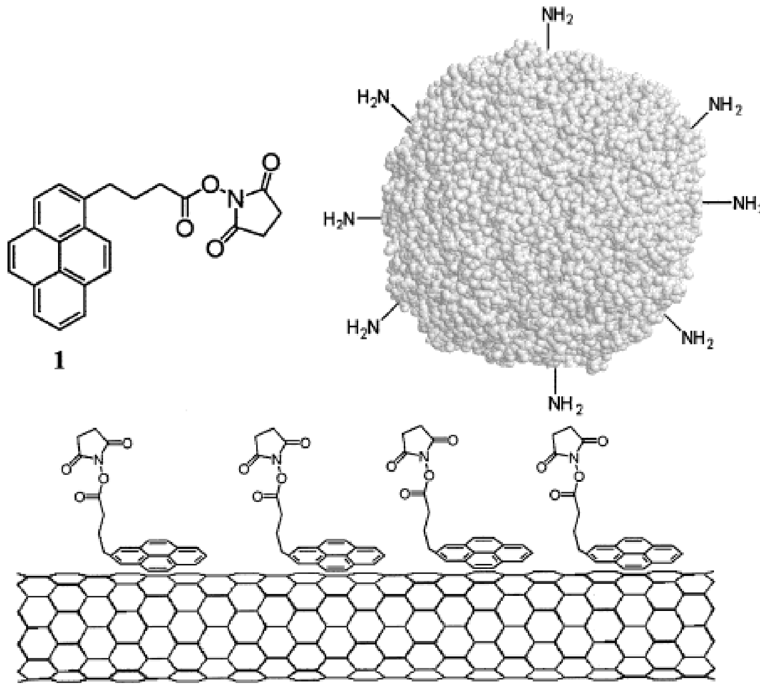
What happens after exposure to water, or to blood? "We want to know how particle size **changes** as it marches through the body." **Size, composition, shape** and **other characteristics** help distinguish the scores of different engineered nanoparticles that exist today. Toxicologists and other scientists studying nanomaterials say these **gaps** make it difficult if not impossible to compare studies and get an accurate picture of how nanoparticles interact with the body.

From workshop designed to identify roadblocks to nanobiotech commercialization

Three examples of surfaces layers or attached molecules that play an important role in the synthesis or properties of nanoparticles



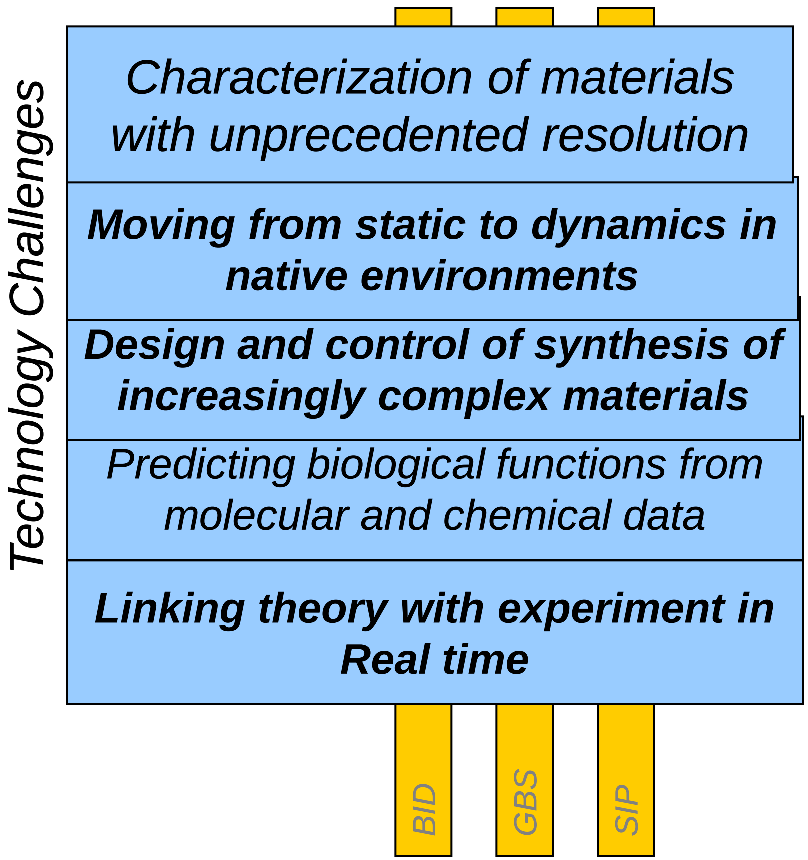




Capability development directions from 2006 EMSL Workshop

Technical challenges that would enable new science identify areas for development

Cross cutting challenges



Science Themes

Workshop links

3d analysis

In situ measurements

Models

Description of NWI from TC201 SC5: Technical Report: Surface Chemical Analysis – Characterization of Nanostructured Materials

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TC201 Surface Chemical Analysis

Scope:

Standardization in the field of surface chemical analysis.

"Surface chemical analysis includes analytical techniques in which beams of electrons, ions, neutral atoms or molecules, or photons are incident on the specimen material and scattered or emitted electrons, ions, neutral atoms or molecules, or photons are detected. It also includes techniques in which probes are scanned over the surface and surface-related signals are detected."

Progress: >50 standards or technical reports published or in progress

Several areas of importance to Nanotechnology ES&H:

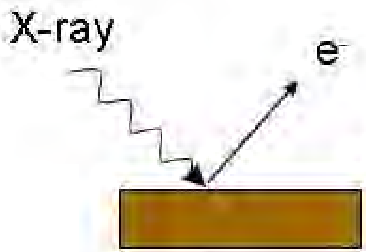
- Terminology
- Newly Approved NWI - Characterization of Nanostructured Materials (balloting closed May 11, 2009)
- SPM

- An inherent property of a nanostructured material, whether a particle, fibre or other object, is the large percentage of the material that is associated with a surface or interface.
- Surface analysis area increasingly used by part of the community to characterize nanomaterials, but are ignored by other parts of the community because they to not inherently have the three dimensional resolution to characterize individual particles
- Technical report addresses two topics:
  - Types of information that surface analysis methods can provide about nanostructured materials.
  - Technical challenges faced when applying surface analysis tools (and often other tools) for characterisation of nanostructured materials.

Major Sections of Technical Report

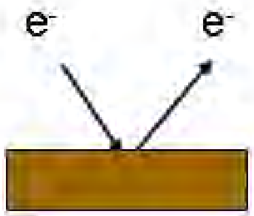
- 4 Challenges in the Characterisation of Nanostructured Materials
- 5 Characterisation of nanostructured materials with surface analysis methods
  - **Nanofilms, layers or dispersions**
  - Nanoparticle Analysis by Surface Analysis Methods
  - **Information about carbon nanotubes**
- 6 General Issues influencing the analysis of nanostructured materials – Information for the Analyst
  - Contamination, Surface Layers and Surface Chemistry
  - Influence of Shape
  - Particle Stability
  - Time and Environment
  - Sputtering
- 7 Specific Issues for nanostructured material analysis using XPS, AES, SIMS and Scanning Probe methods
  - Issues related to application of XPS, SIMS, AES and SPM to nanomaterials

Overview of electron spectroscopies XPS and AES



X-ray photoelectron spectroscopy

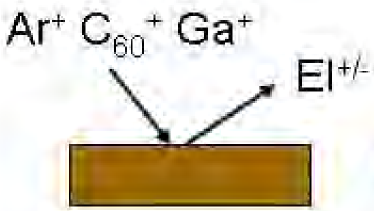
Lateral Resolution ≈ 2 μm
Information Depth ≈ 10 nm
Depth Resolution ≈ 1 nm



Auger electron spectroscopy

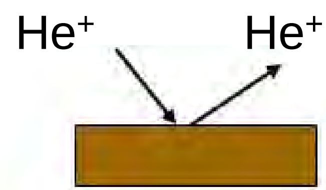
Lateral Resolution ≈ 10 nm
Information Depth ≈ 10 nm
Depth Resolution ≈ 1 nm

Overview of ion based surface methods - SIMS and LEIS



Secondary ion
mass spectrometry

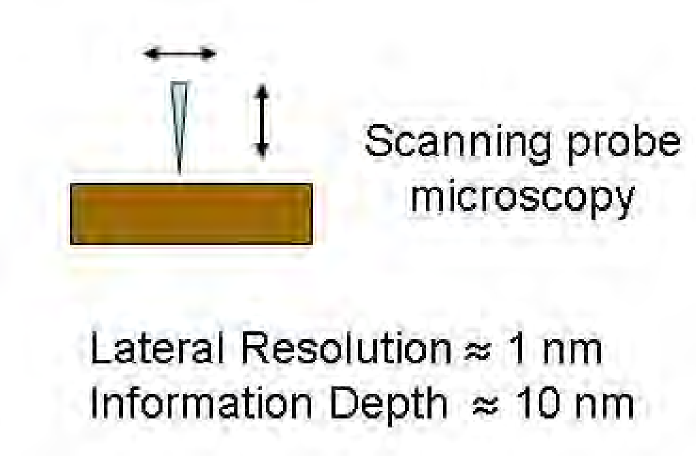
Lateral Resolution (inorganic) ≈ 50 nm
Lateral Resolution (organic) > 200 nm
Information Depth ≈ 1 nm
Depth Resolution (inorganic) ≈ 1 nm
Depth Resolution (organic) ≈ 10 nm



Low Energy
Ion Scattering

Lateral resolution » 100 mm
Information Depth » 10 nm
Depth Resolution » 0.2 nm

overview of the scanning probe microscopy



Information obtained XPS regarding nanoparticles

- Contamination,
- Particle coatings and thickness
- Oxidation rates
- Particle Size
- Electrical Properties of Particles

Information available from SIMS of Nanoparticles

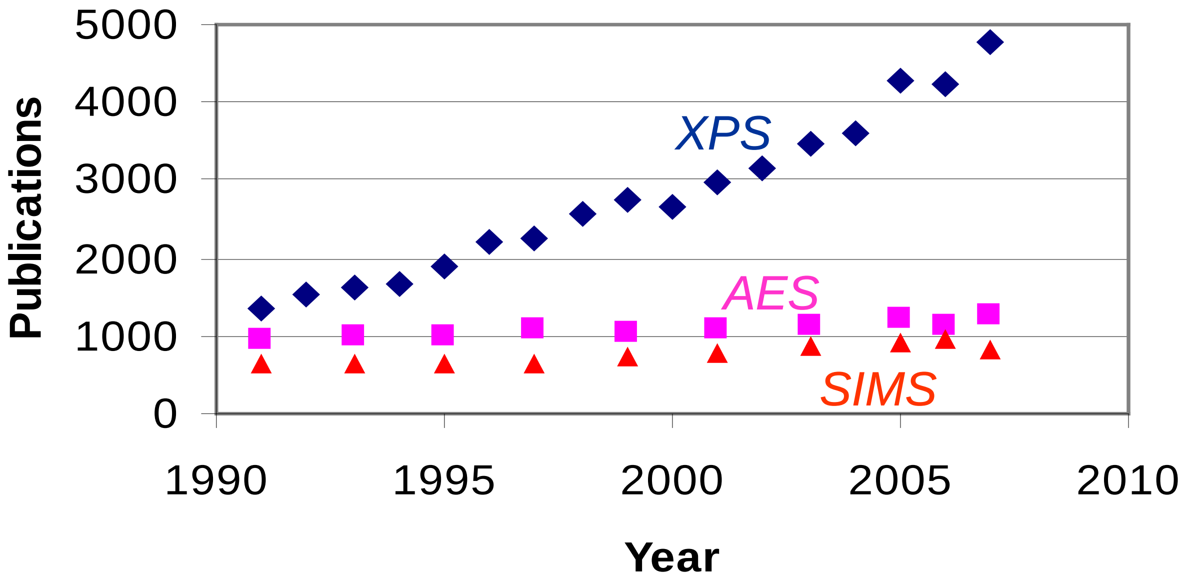
- Contamination and Layer structure
- Nanoparticle Characterization – composition depend on formation condition
- Nanoparticle Formation

Information available about CNTs

- Growth processes
- Doping effects, surface functionalization, charge transfer
- Contamination

Application of XPS is particularly grown rapidly at least in part due to application to nanostructured materials

Numbers of publications by year with XPS, SIMS or AES as a topic



Web of Science topical search:

TS=(SIMS or "secondary ion mass spectrometry")

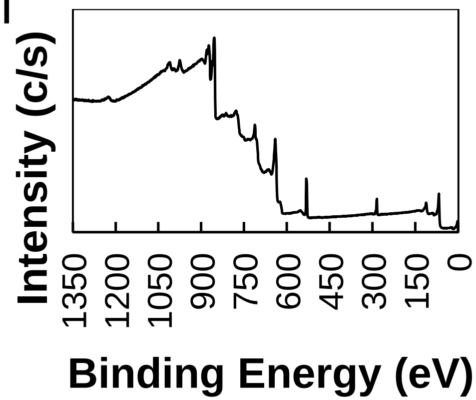
TS=(AES or "Auger electron spectroscopy")

TS=(XPS or "x-ray photoelectron spectroscopy")

Update of graph prepared by Cedric Powell for JVST A 21(2003) S42

Nanostructure influences XPS signals in several ways

- Peak intensities and relative peak intensities of
  - peaks for different elements
  - different peaks for the same element
  - variation as a function of emission angle
- Peak energies
  - binding energies of peaks
  - value of the Auger parameter
- Background signals from electrons that have lost energy.

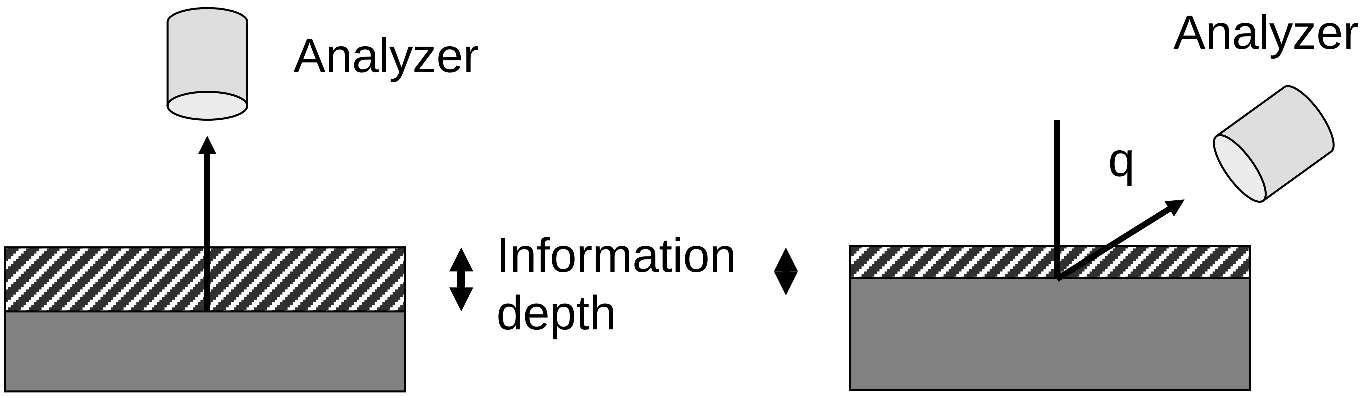


Using this and other information, XPS can determine

- Surface and "bulk" composition (and sometimes functional groups)
- Layer thickness and structure
- Particle coatings
- Particle size (sometimes when it cannot be obtain by other methods)
- Surface segregation or enrichment

Kinetic energy and detection angle impact information depth

a)

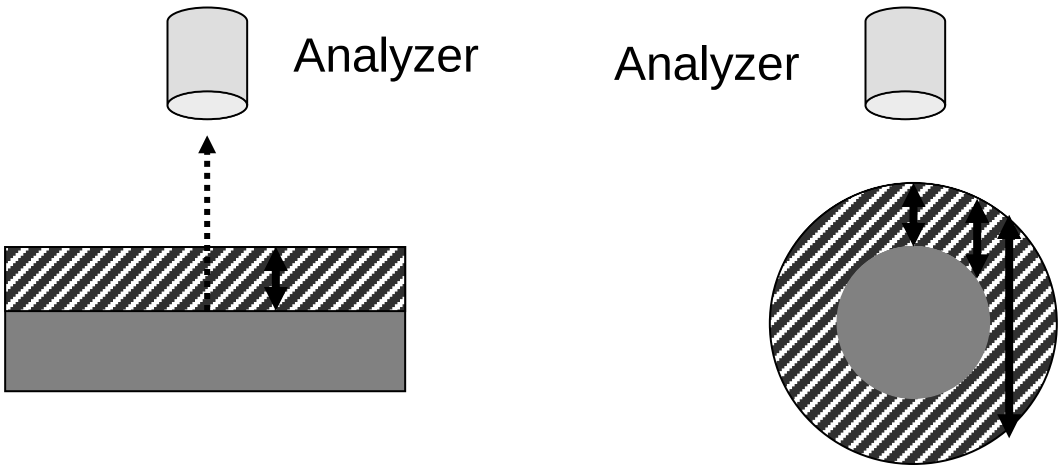


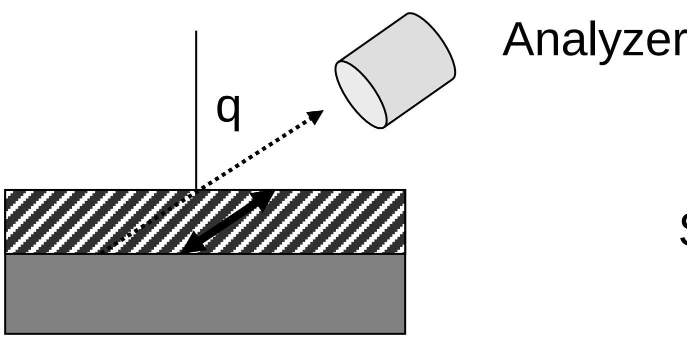
b)

Information depth
- Normal emission
- High kinetic energy

Information depth
- High angle emission
- Low kinetic energy

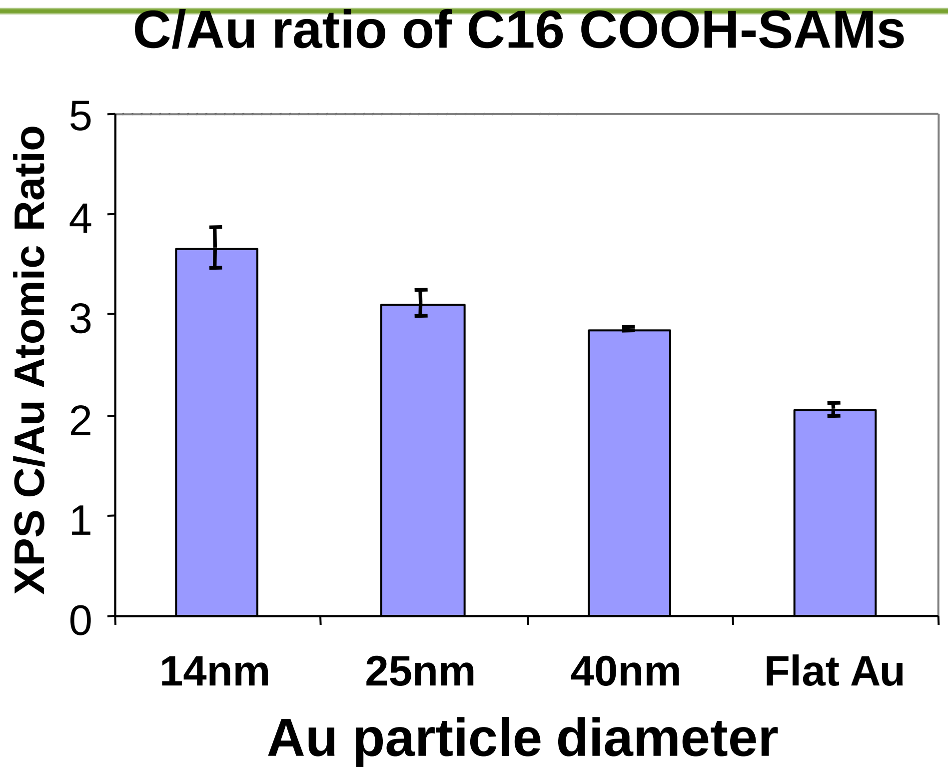
Thickness concepts for films can be extended to particles





Shard correction Factor = 0.67
"Magic Angle" $\cos(45^0) = 0.71$

$$\ln (1+R_{exp}(q)/R_0) = d/L\cos q$$



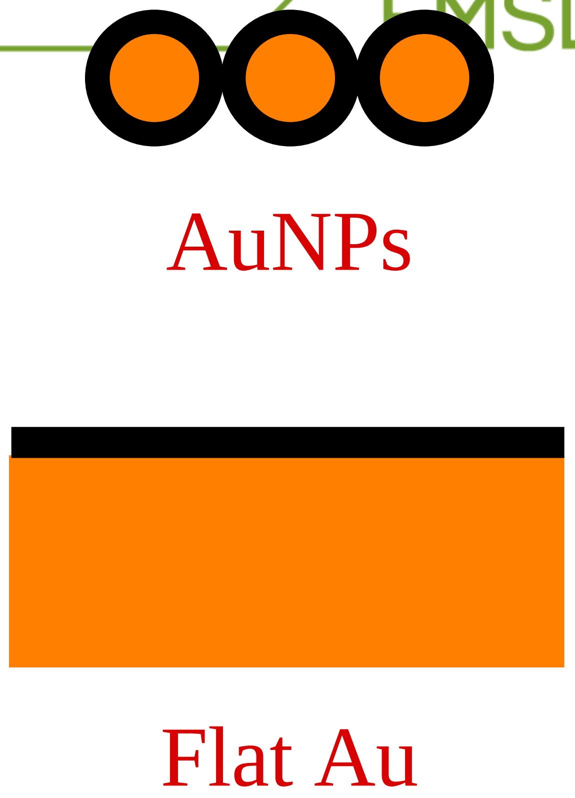
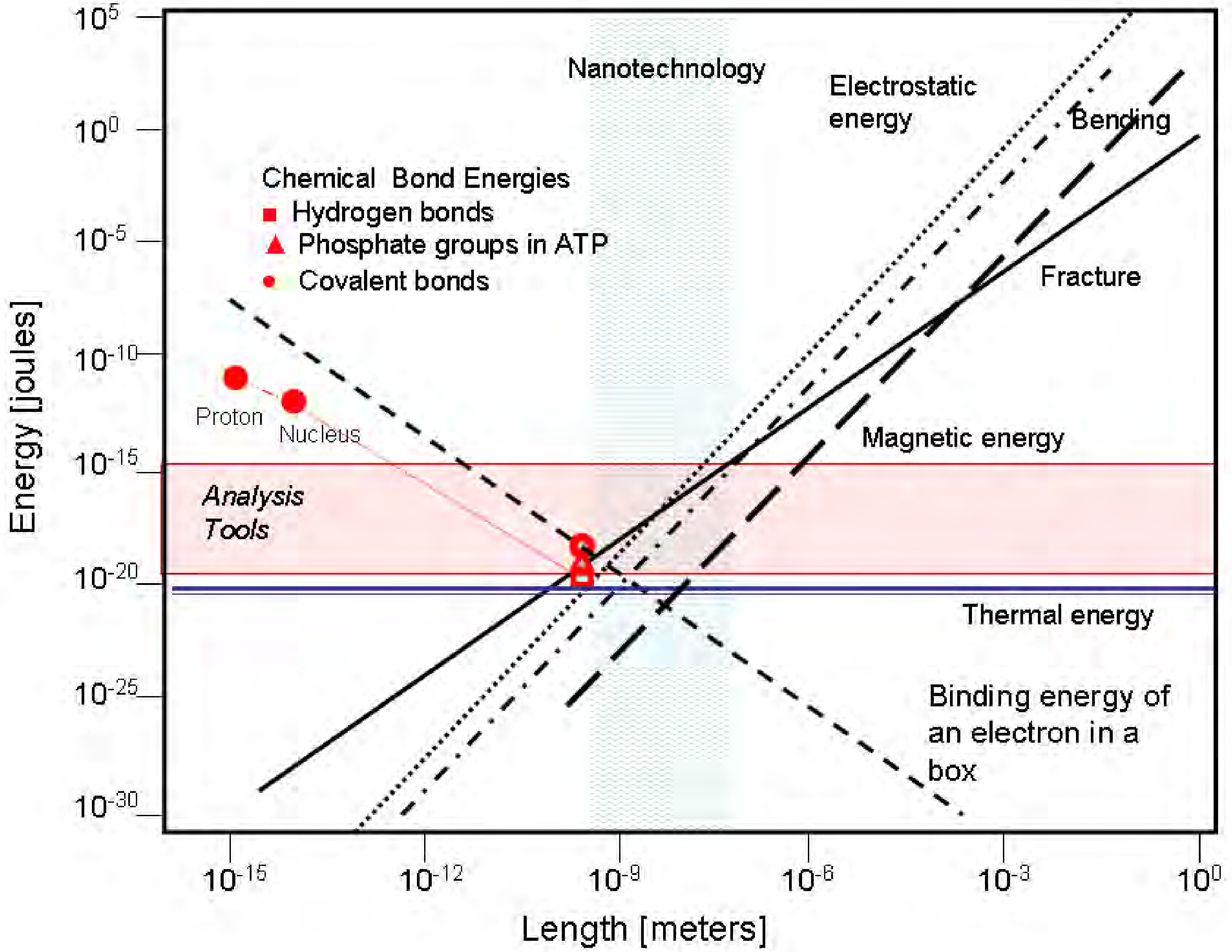


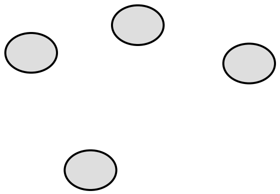
Figure 9 – The C to Au elemental composition ratio measured by XPS for SAM terminated Au nanoparticles as a function of particle size. As the particle size decreases the relative amount of C sensed increases even with the coating thickness (a C16 COOH terminated SAM) remains constant. When the particle size is known the intensity ratio can be used to determine coating thickness.

Different types of particle energy converge at the nanometer size

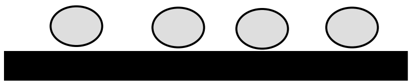


Variations in thermal, chemical, mechanical, magnetic and electrostatic energies as a function of the size of an object. For objects with sizes associated with nanotechnology (and many biological processes) many of these energy scales converge providing increased opportunities for coupling of different excitation modes.

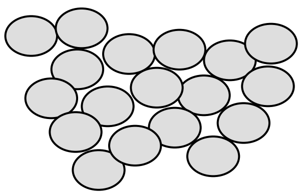
Some properties of nanoparticles change as they are grouped or supported



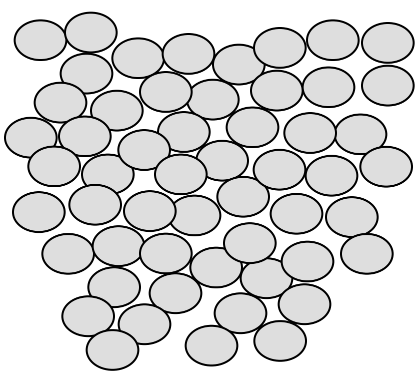
Isolated Nanoparticles



Supported nanoparticles

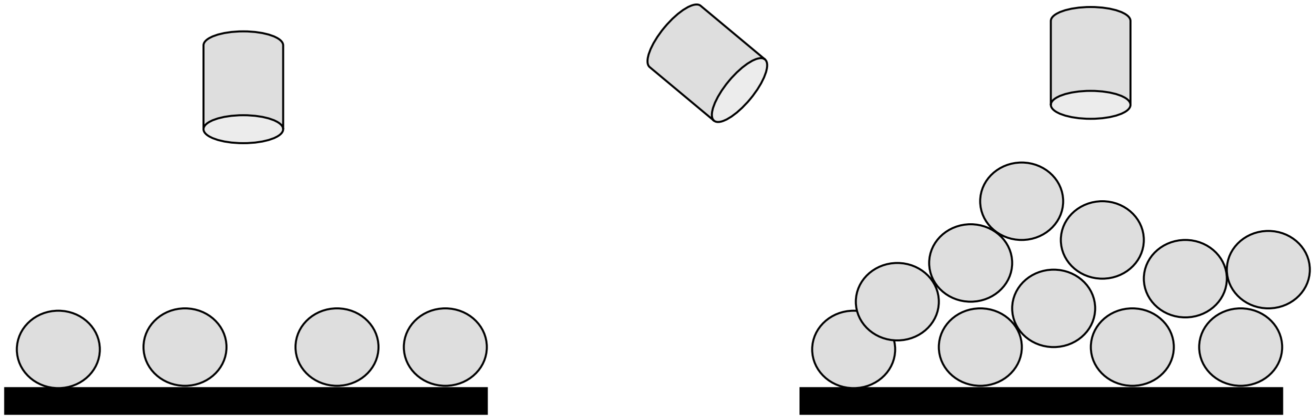


Aggregated or compacted nanoparticles

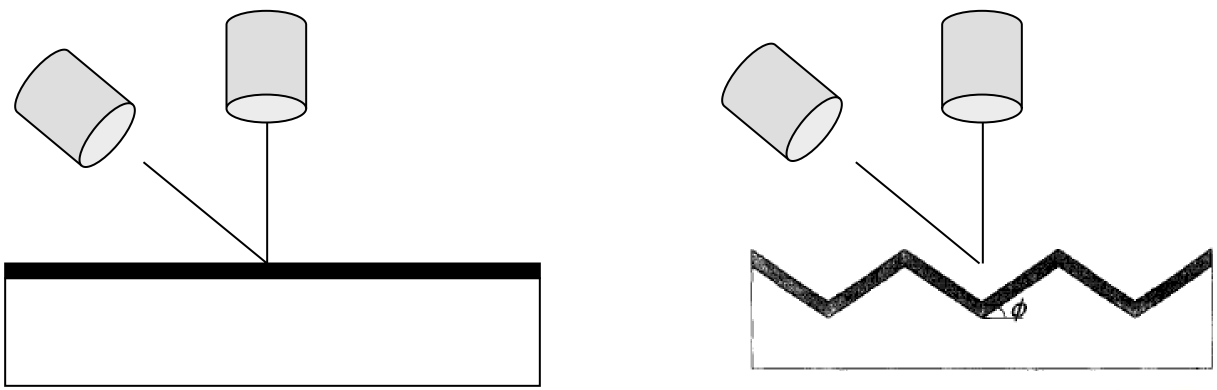


Compacted Powder

How do I mount the sample and collect the data?



Topographic correction or “Magic” angle?



Shard et. al. Surface and Interface Analysis, 2009 (DOI 10.1002/sia.3044)
Gunter et al. Applied Surface Science, 1997. **115**(4): p. 342-346.
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Status

- Need identified and concept developed in Fall 2007
- Rough draft of document prepared and proposed as NWI in Fall of 2008
- Draft revised and NWI ballot initialed in February 2009
- NWI approved in May 2009 – status working draft (stage 20) 12 experts identified
- Additional experts or other /feedback requested
- Requesting input from experts (and additional experts)
- Plan updated draft in Fall 2009 which should be become Committee Draft

Contact Don Baer (don.baer@pnl.gov)

Summary and Opinions

- Characterization of nanostructured materials is increasingly **important**
- Characterization of these materials presents many **challenges** some of which are **not fully recognized** by parts of the research community - including the impact of surface and interface contamination
- Particularly important are **particle stability**, the impact of sample **history**, the **environment** and previous **processing**, and **time dependent** properties – need to understand/improve **sample handling protocols**
- **Complementary** analysis tools and theory are often essential. The need for **expert application**, **theory (modeling)** and **multiple tools** creates knowledge and access issues (surface tools under used and need to be applied with increased sophistication)
- Great need for **real-time** measurements in the environment of interest (**in situ** or **operando** methods)
- In some cases **new concepts** and **new tools** are needed to understand and characterize the fundamental nature of nano-structured materials