NANO Science, Engineering and Technology

September 15-16, 2003

Interagency Grantees Meeting/Workshop - Nanotechnology and the Environment: Applications and Implications

Small particle chemistry:

Reasons for differences and related conceptual challenges

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Pacific Northwest National Laboratory
Richland, WA

P. G. Tratnyek
Oregon Health and Sciences University
Beaverton, OR

Topics

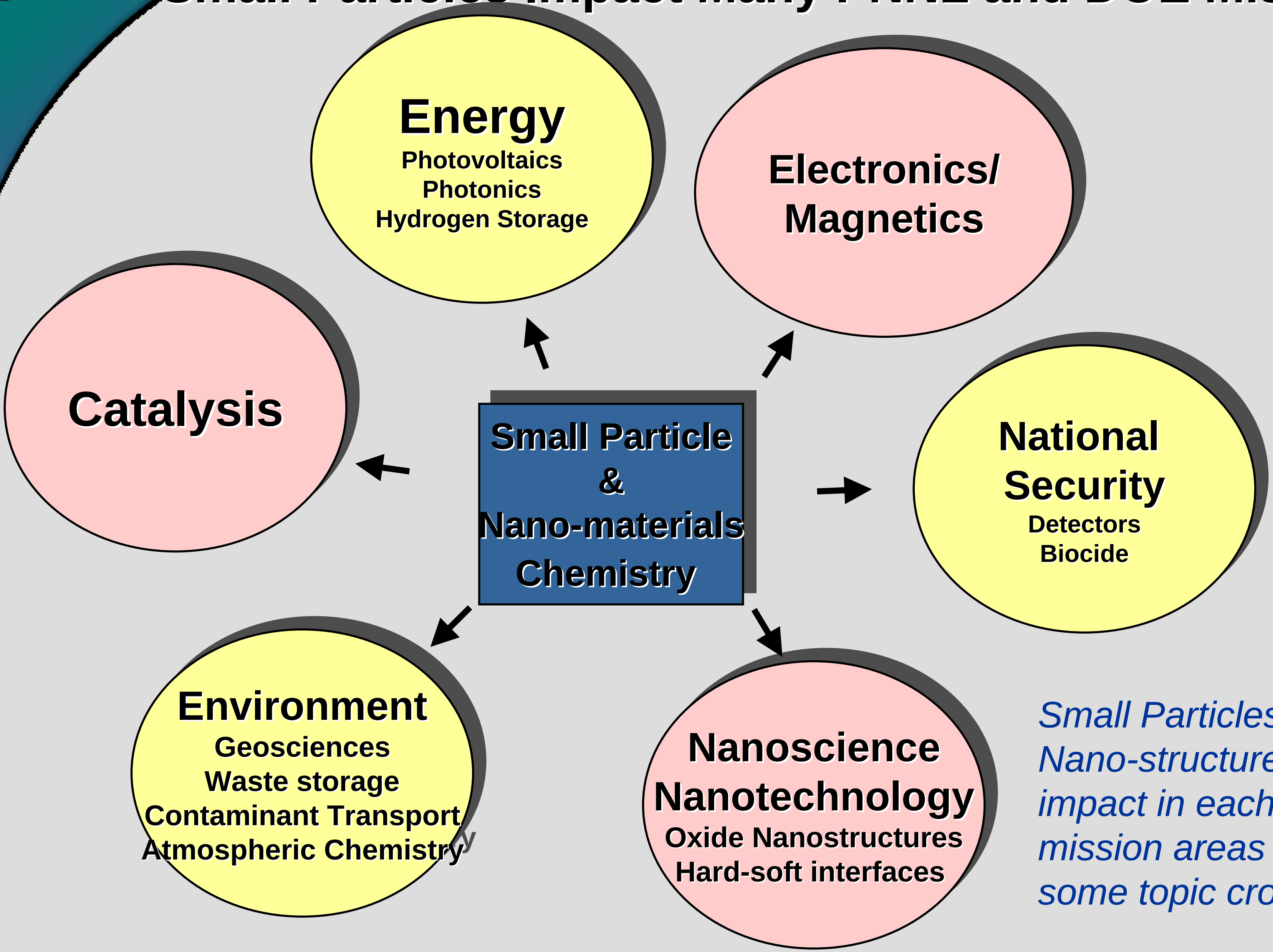
- **Chemical properties of small particle and nano-structured materials** - natural and manmade – important for PNNL Missions most with environmental implications
- **Characterization and Challenges** in making, handling and characterizing nanoparticles – *nanoparticles may have an impact on the environment, but the environment also impacts the nature of the nanoparticles*.
- **Different ways that small** or nano-structure **makes a chemical difference**.
- **Specific Program**: Reaction Specificity of Nanoparticles in Solution: Application of the Reaction of Nanoparticulate Iron with Chlorinated Hydrocarbons and Oxyanions

Pacific Northwest National Laboratory

- Located in Richland, Washington
- Approximately 3,500 employees
- We deliver breakthrough science and technology to meet key national needs with a large environmental focus:

Fundamental Science	Environmental Science and Technology
Energy Future	National & Homeland Security

Small Particles Impact Many PNNL and DOE Missions



Small Particle & Nano-materials Chemistry

Energy
Photovoltaics
Photonics
Hydrogen Storage

Electronics/ Magnetics

Catalysis

National Security
Detectors
Biocide

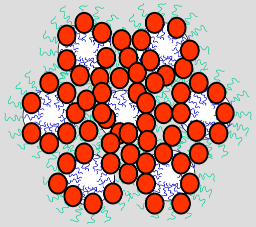
Environment
Geosciences
Waste storage
Contaminant Transport
Atmospheric Chemistry

Nanoscience Nanotechnology
Oxide Nanostructures
Hard-soft interfaces

Small Particles and Nano-structures have impact in each DOE mission areas and some topic cross

Nano-structured Reactive Materials Systems (Nano-chemistry)

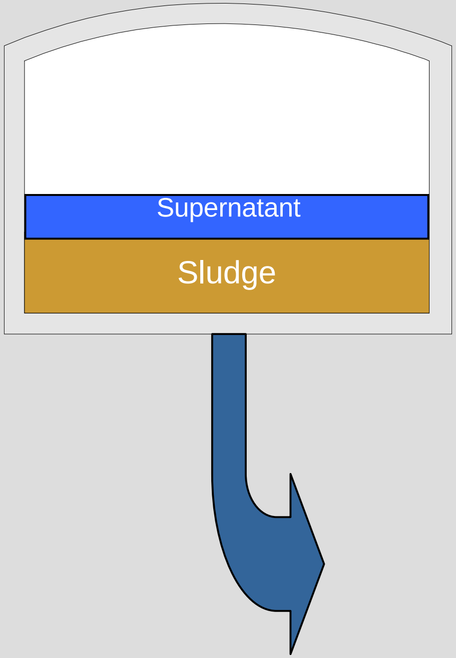
- Control of the chemical and physical properties of hierarchal materials structures containing nano-sized components to control and optimize material properties and chemical reactivity
- Application Areas
  - Catalysts for fuel cells, bioprocessing, waste reduction and the chemical industry
  - Inexpensive photovoltaic and other energy conversion devices
  - Highly selective sensing materials and systems
  - Structure optimized for energy transport
- Science Issues
  - Tune nanomaterial physical and chemical properties
  - Place structures in appropriate hierarchal environments
  - Integrate structures into mesoscopic and macroscopic systems
  - Develop theory and computation approaches to predict properties



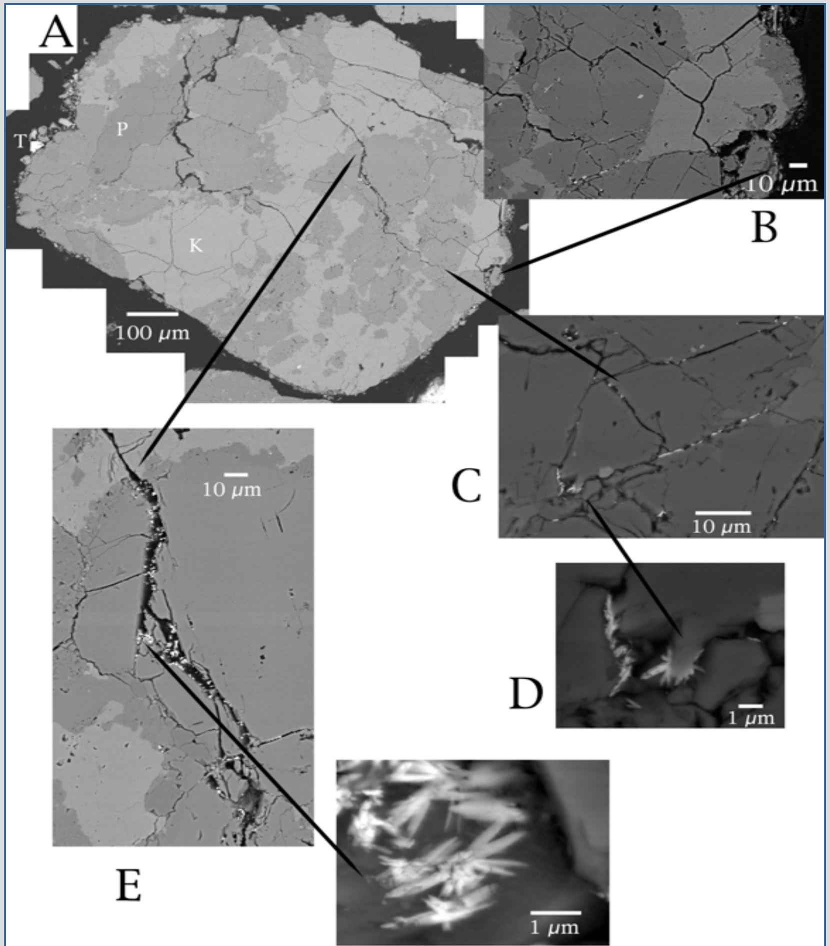
Small Particles Important for Contaminant Transport in "Natural" System

Tank Wastes at Hanford

40,000,000 Gallons

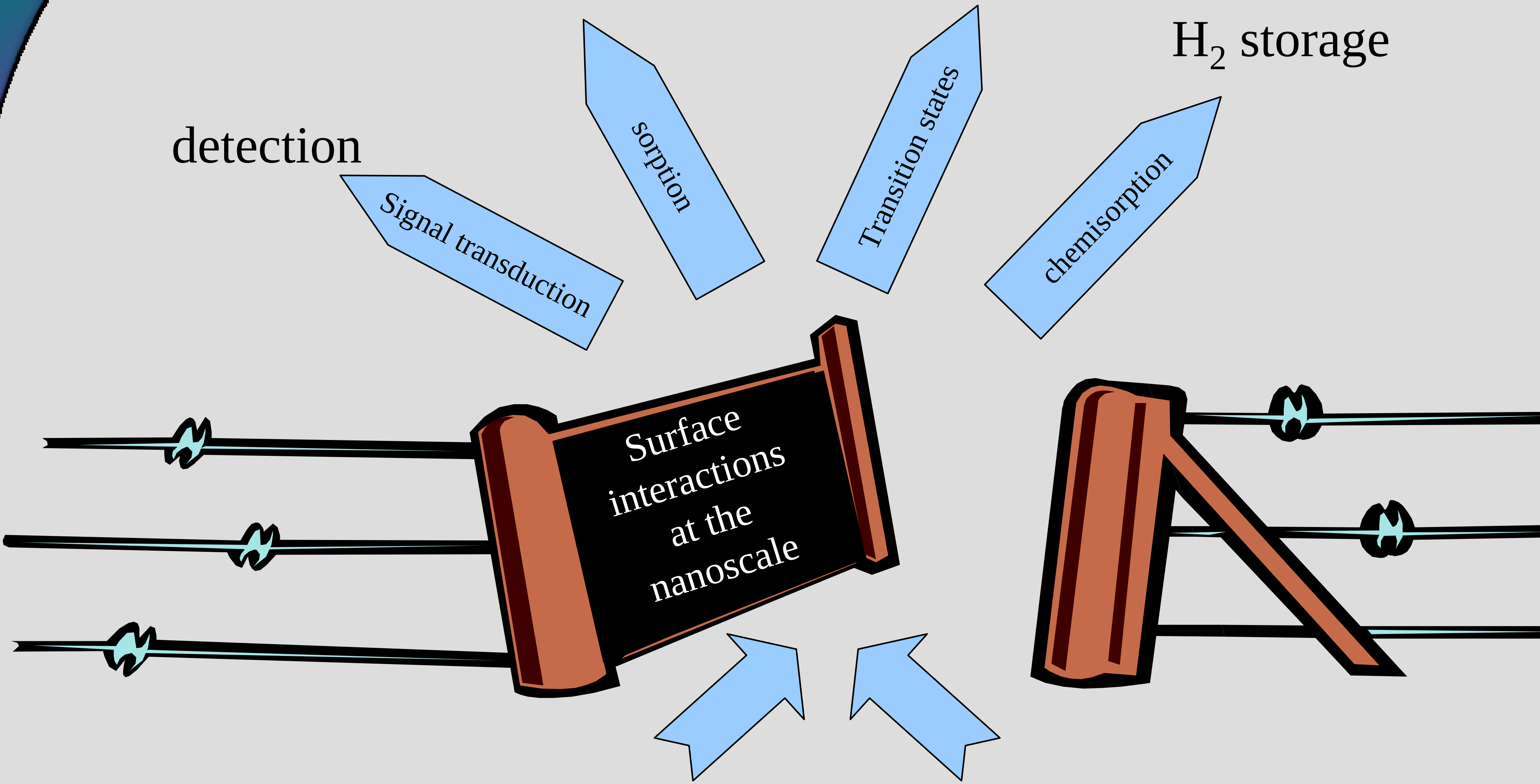


U(VI) Micro- and Nano-precipitates Exist within Grain Fractures of Quartz and Feldspar in BX-102 Sediment 61



One portion of the Nanoscience and Nanotechnology Landscape

Control of nanostructure is a gateway



detection

pre-concentration

catalysis

H_2 storage

Signal transduction

sorption

Transition states

chemisorption

Surface interactions at the nanoscale

synthesized nanostructures

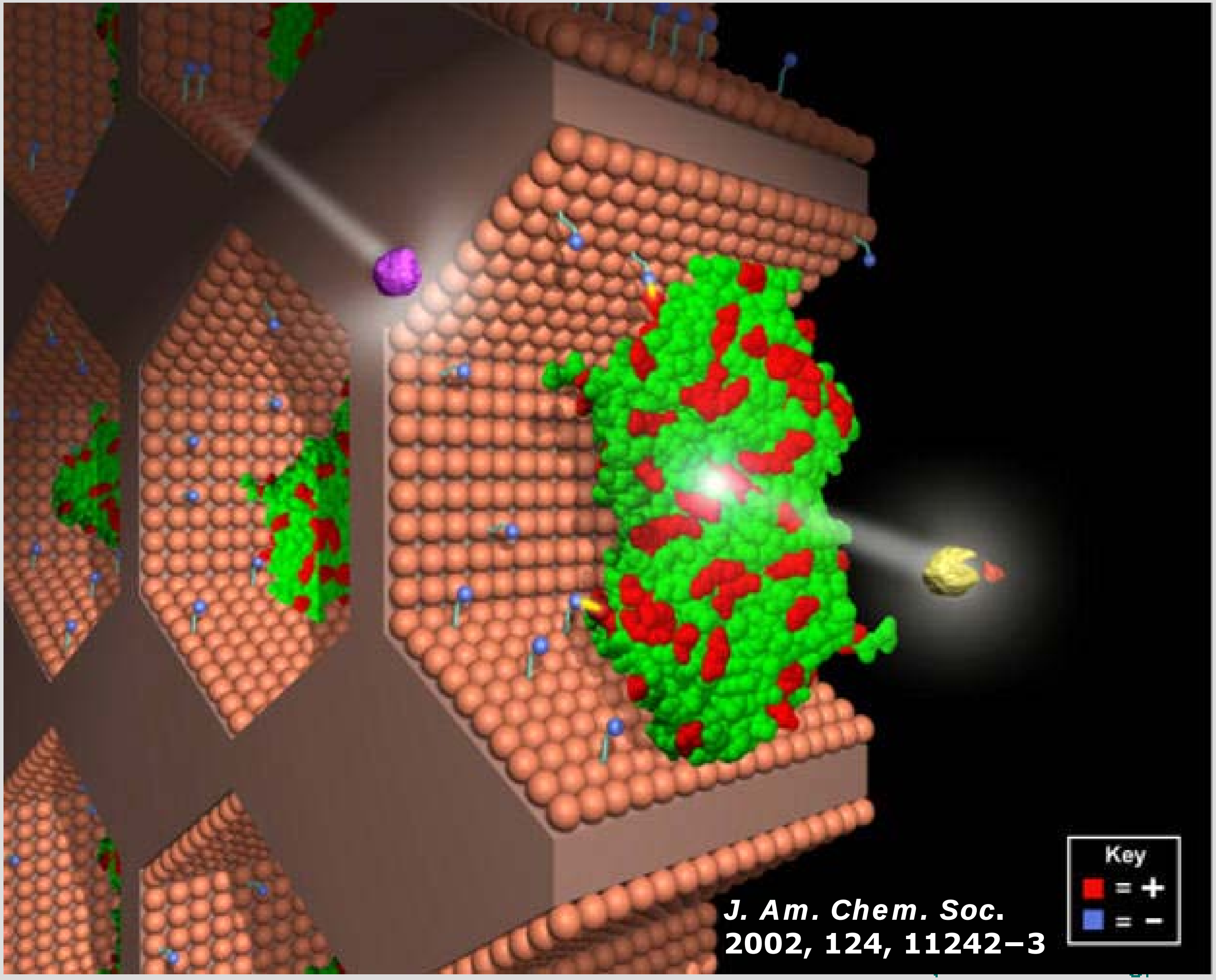
nanobiological machines

Harnessing Enzymes: An Application of Proteins

Stable enzymes entrapped in nanopores may one day be routinely used to inactivate pollutants.

Enzymes in this environment are stable for extended periods of time.

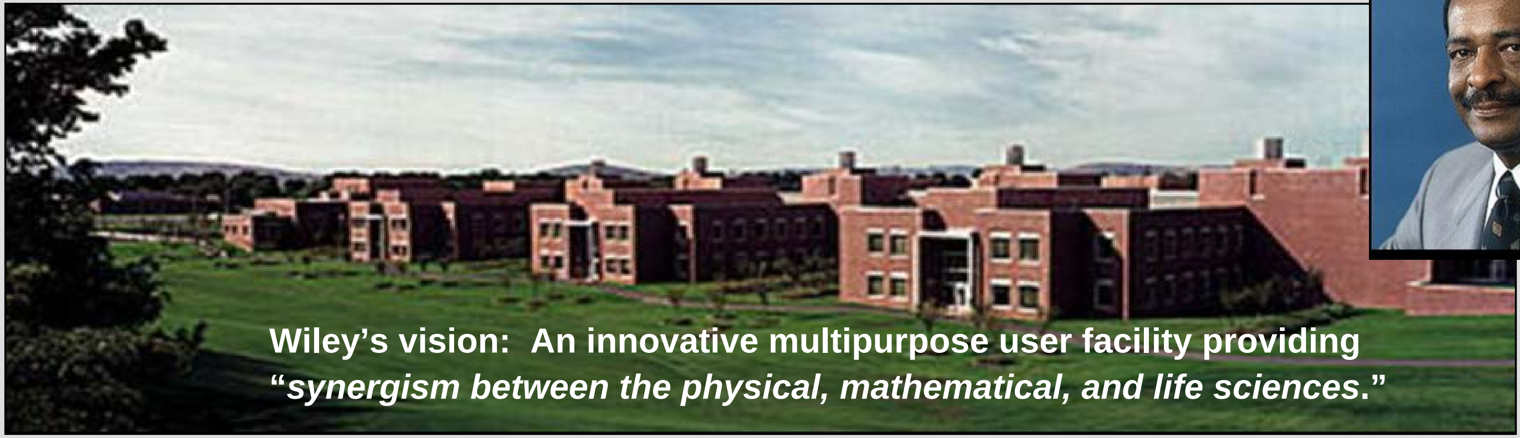
Sensors, catalysts and separations



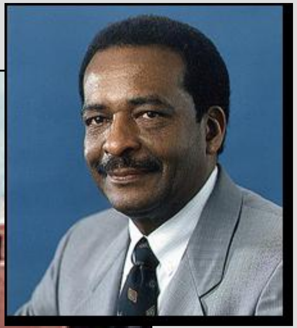
J. Am. Chem. Soc. 2002, 124, 11242–3

Pacific Northwest National Laboratory

Environmental Molecular Sciences Laboratory National User Facility



Wiley's vision: An innovative multipurpose user facility providing "*synergism between the physical, mathematical, and life sciences.*"



EMSL Facilities

- Chemistry and Physics of Complex Systems
- Environmental Spectroscopy & Biogeochemistry
- High Field Magnetic Resonance
- High Performance Mass Spectrometry
- **Interfacial & Nanoscale Science**
- Molecular Science Computing

Signature Characteristics

- Integration of **theory, modeling**, and simulation with **experiment**.
- **Multidisciplinary** teams and collaborative mode of operation to solve major scientific problems of interest to DOE and the nation.
- Teams who develop extraordinary **tools and methodologies**.

Topics

- **Chemical properties of small particle and nano-structured materials** - natural and manmade – important for PNNL Missions most with environmental implications

- Challenges in making, handling and characterizing nanoparticles – *we need to learn how to characterize nano systems more completely and adequately*
  - *Emphasized comments made by Bob Hwang, Karen Swider-Lyons and Andrea Belcher. Highlights importance of creating and applying of new facilities including the new generation TEM*.

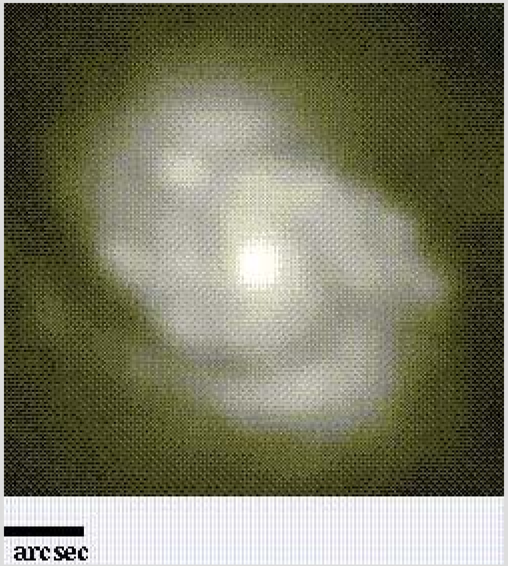
- **Different ways that small** or nano-structure **makes a chemical difference**.

- **Specific Program**: Reaction Specificity of Nanoparticles in Solution: Application of the Reaction of Nanoparticulate Iron with Chlorinated Hydrocarbons and Oxyanions

Calibrating the state of our understanding

Nebula M100

Kitt Peak
1.1 M



My view of the state of our understanding of nanoparticle chemistry?

Calibrating the state of our understanding

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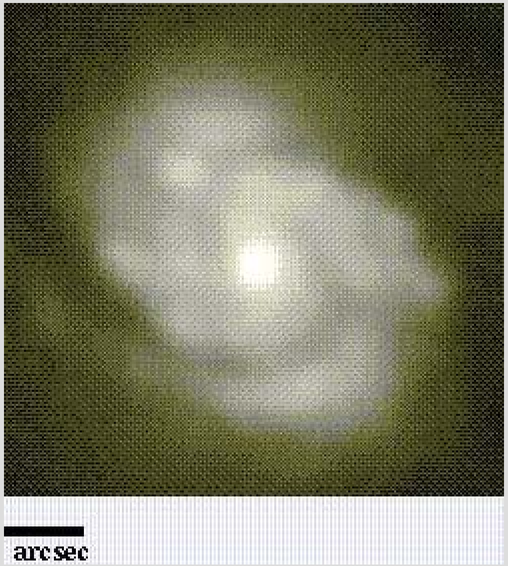

Hubble
Space
Telescope

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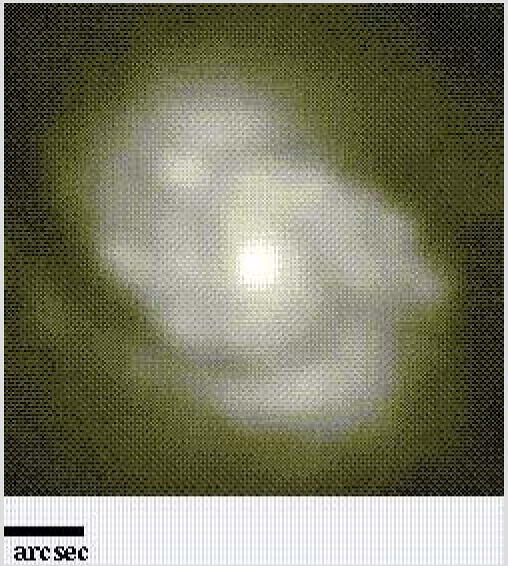
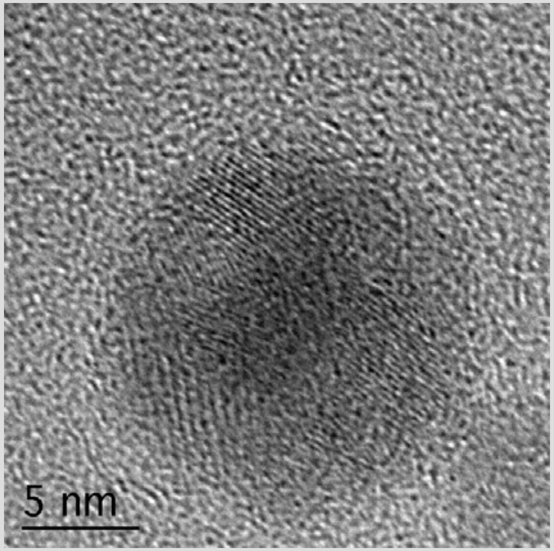


Hubble
Space
Telescope

Nanoparticle Images

TEM of
Fe



?

Calibrating the state of our understanding

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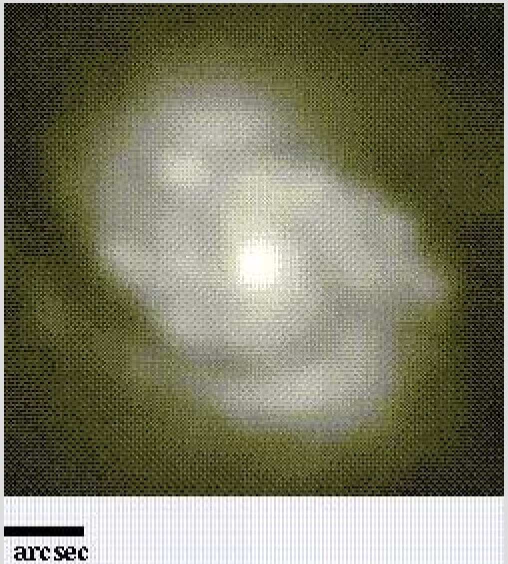

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Nanoparticle Images

TEM of
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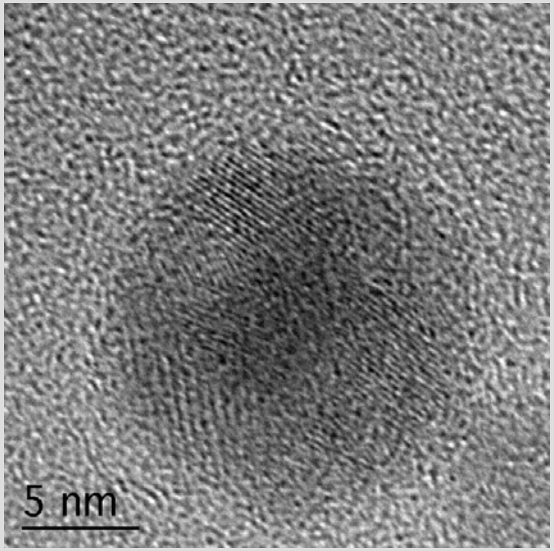
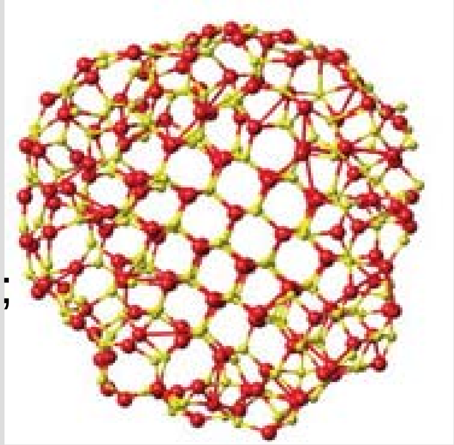


Molecular Dynamics ZnS

Need more and advanced **tools**; greater development and application of **theory and modeling**; expand **conceptual framework**



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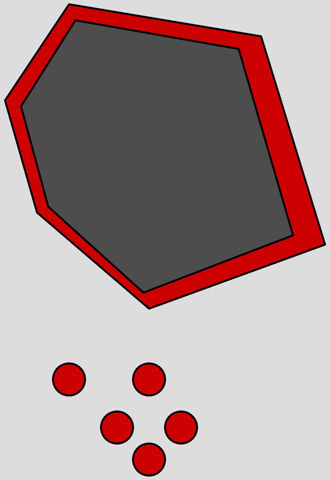
THE REACTION SPECIFICITY OF NANOPARTICLES IN SOLUTION:

Application to the Reaction of Nanoparticulate Iron and Iron-Bimetallic Compounds with Chlorinated Hydrocarbons and Oxyanions.

Evidence that nanoparticles change the iron induced reduction of CCl_4 from partial reduction toward full removal of the Cl:

From

$CCl_4 + H^+ + Fe^0 \rightarrow CHCl_3 + Fe^{+2} + Cl^-$



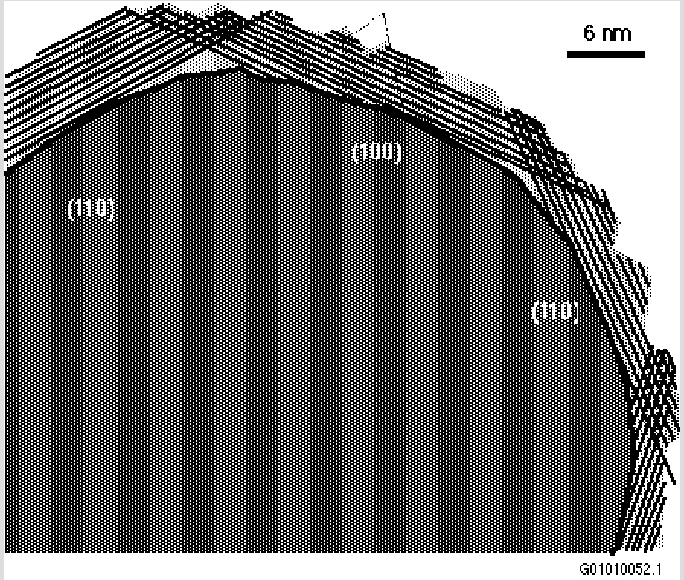
To

$CCl_4 + 4H^+ + 4Fe^0 \rightarrow CH_4 + 4Fe^{+2} + 4Cl^-$

No fundamental understanding of the process.

Understanding the properties of Fe nanoparticles presents a host of challenging questions and problems

- What size range or structure is of importance?
- How small of a nanoparticle contains a metallic core?
- What is the structure of any metal in a nanoparticle?
- What is the structure of the oxide on a nanoparticle and how does it change with particle size?
- How do environmental effects alter nanoparticle structures and change reactivity?
- Where do reduction reactions take place and how does this change with particle size or structure?



Schematic representation of the different Fe(0) iron surface planes and the growth of compressively strained oxide lattices (adapted from Kwok et al. 2000).

Three (of several) Senses of Small

What do we we mean by small particle and why does their chemistry change?

- **Size and surface area effects**

1 nm – 100 nm **Fundamental materials properties remain** the same but size, shape and surface area alter some behaviors work function, solubility, chemical potential, contaminate sorption

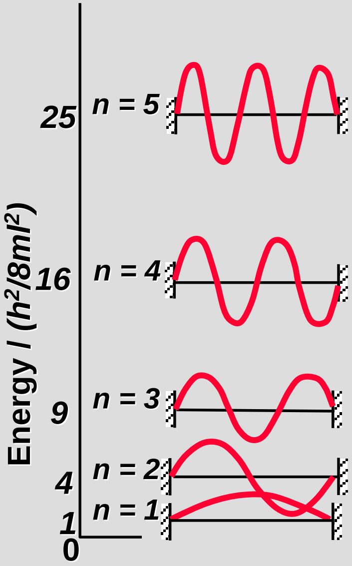
- **Critical Size and Characteristic Length Scale**

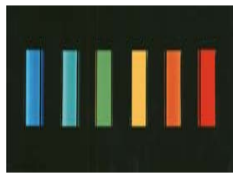
Interesting or unusual properties because the **size of the system approaches some critical length** (includes quantum effects). **Many characteristics** of material may have normal or nearly **normal** behavior

- **New (Non-extensive) Properties**

Systems not large enough to have extensive properties. Particles become effectively polymorphs of “bulk” materials and statistical homogeneity may not be valid.

- Kelvin equation for solubility
- Gibbs-Thompson relation for chemical potential





size ≈ ς ≈ d

ς= correlation length

d = range of intermolecular forces

Nanoparticle Energy 1

Significant effects are predicted for nanosized particles when materials properties are well defined and constant

Gibbs-Thompson relation as an estimate of dependence of particle energy on size

$$\mu(r) - \mu(\infty) = 2\mathrm{K}\Omega/r$$

K= surface free energy, A = molecular volume
r = particle radius

This effect becomes significant at for metals at 2-3 nm

Assumes that surface free energy is independent of size!

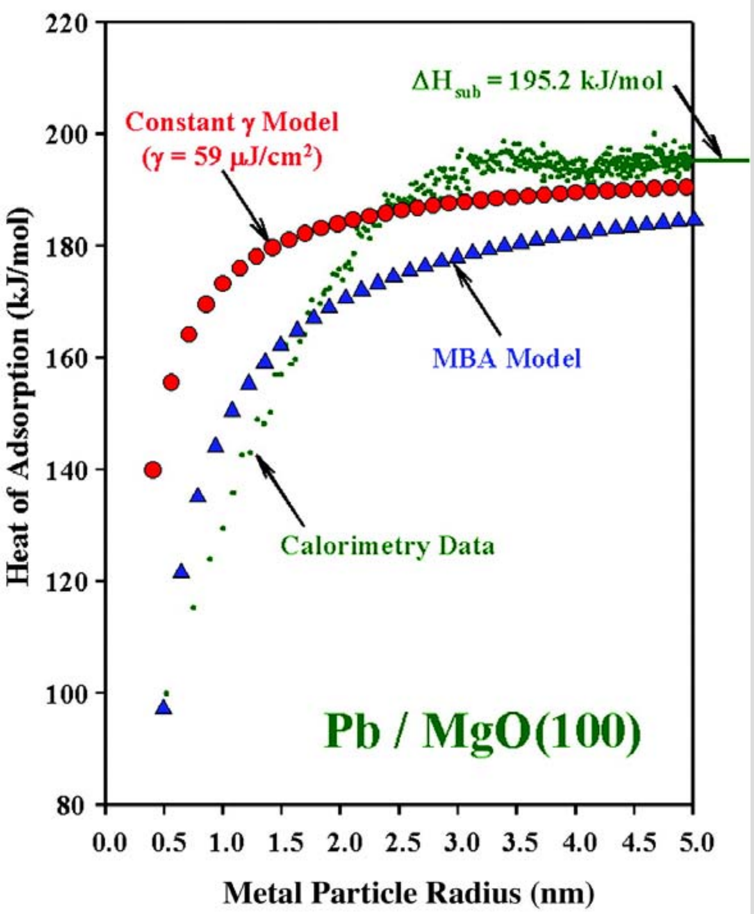
Nanoparticle Energy 2

Often the materials properties are not constant.

Calorimetric measurements show that the energy dependence of supported Pb particles vary much more quickly than predicted by the Gibbs-Thompson relationship.

“This shows that the surface energy increases substantially as the radius decreases below 3 nm.”

C.T Campbell et. al. Science 298 (2002) 811-814



Nanoparticle Energy 3

The materials properties may not be uniquely defined They may depend on the environment.

The Molecular Theory of Small Systems
Faraday Lecture, 1983
R. S. Rowlinson, Chemical Society Reviews, Vol 12, (1983) 251-265

For small systems, some of the thermodynamic functions of importance, **pressure** and **energy density** are not uniquely defined.

Small systems can be defined when the system **size** ≈ ς ≈ **d** ≈ **l** **(often ≈ nm)**

ς= correlation length; d = range of intermolecular forces; l = thickness of an interface

For systems smaller than ς **thermodynamics and statistical mechanics lose their meaning.**

A Different Approach to Nanothermodynamics

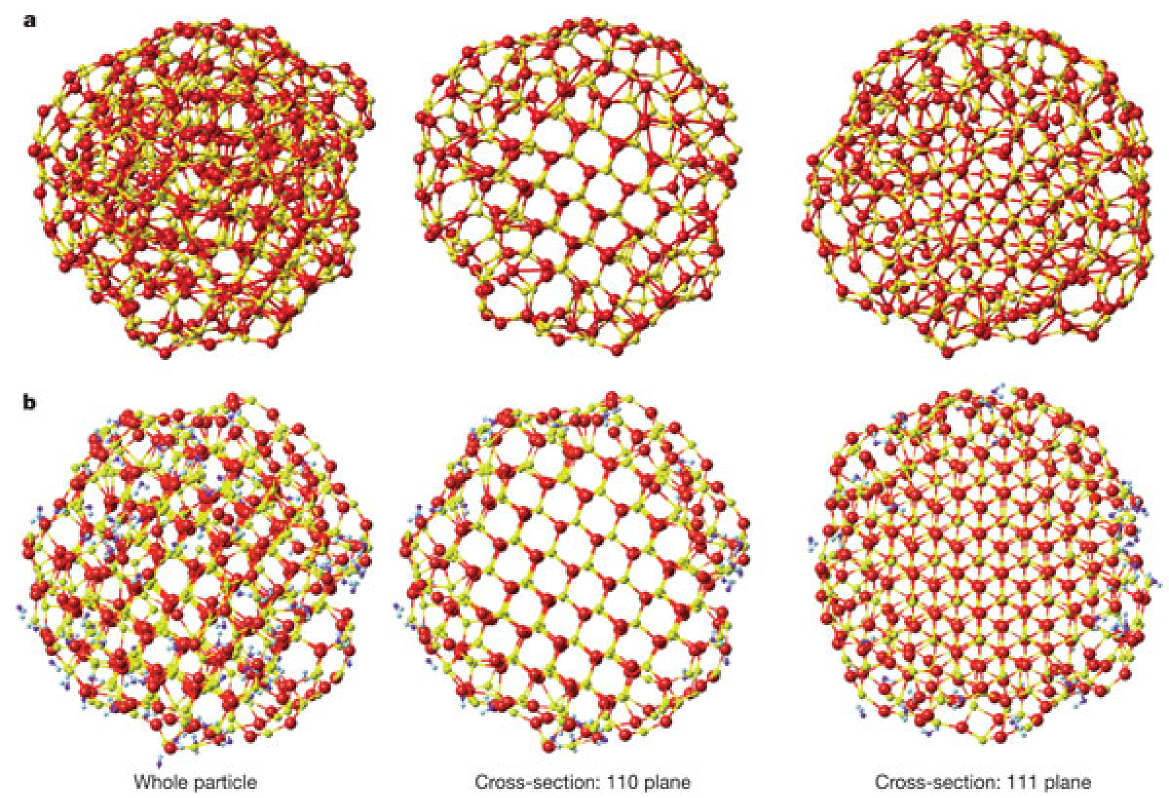
Terrell L. Hill, Nano Letters Vol 1 (2001) 273-275

“In contrast to macrothermodynamics, the **thermodynamics of a small system will usually be different in different environments**.”

Nature **424, 1025 - 1029 (28 August 2003);**

Water-driven structure transformation in nanoparticles at room temperature

HENGZHONG ZHANG*, BENJAMIN GILBERT*, FENG HUANG & JILLIAN F. BANFIELD



Vacuum

With $H_2$0
on surface

Should an environmental influence on nano-particle structure be a surprise?

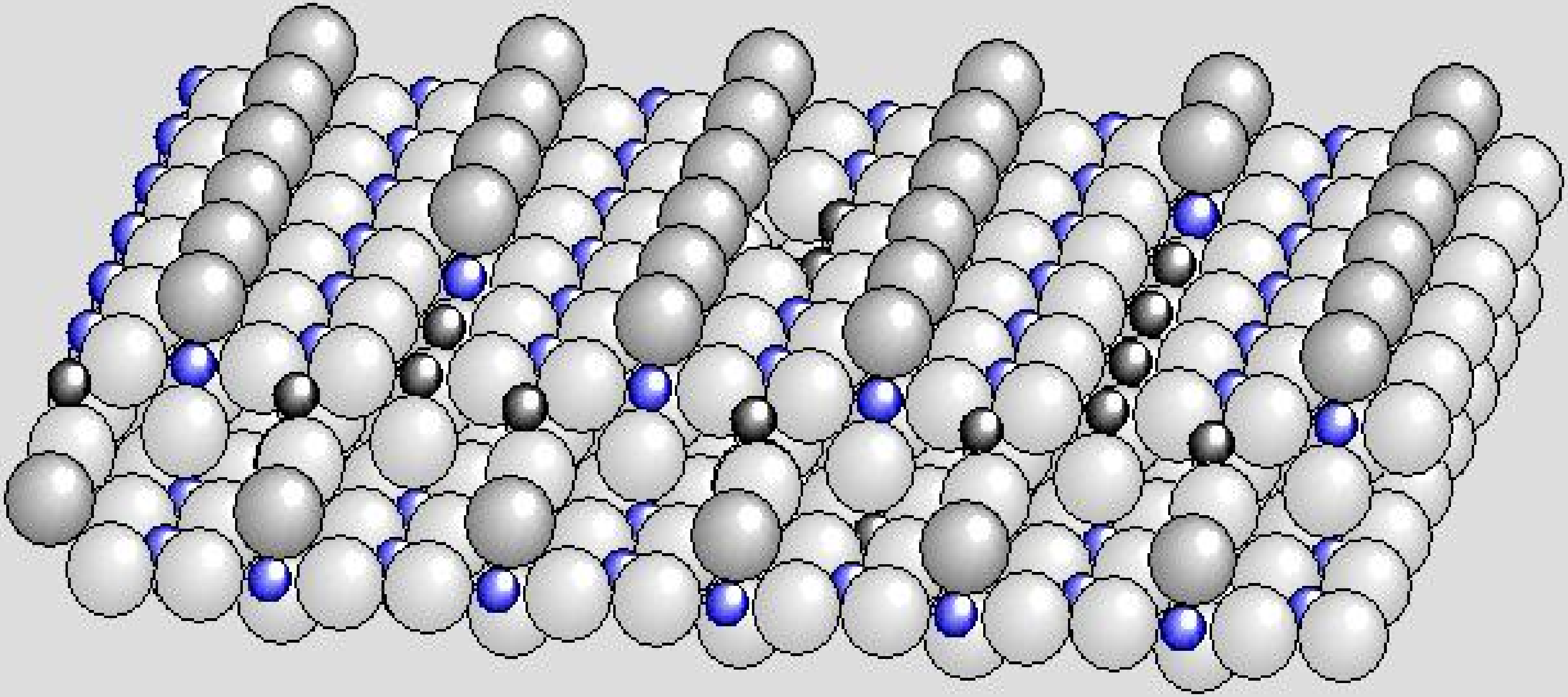
No - Consistent with theory and even experiments on “bulk” surfaces.

Rutile TiO_2 [110] Surface

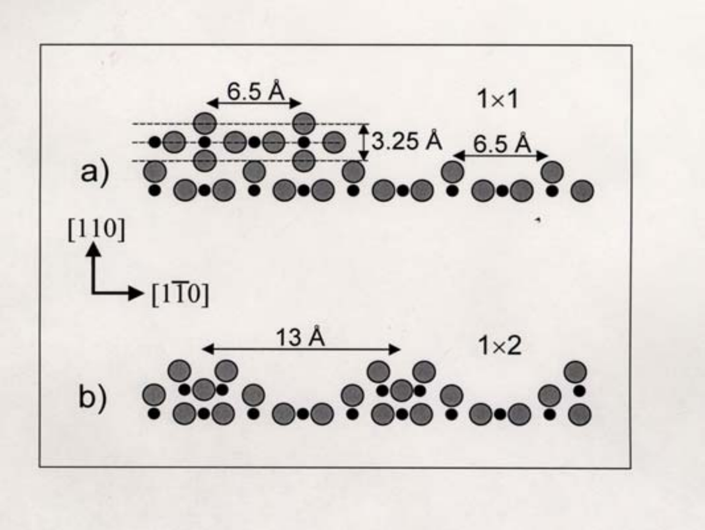
With defect sites

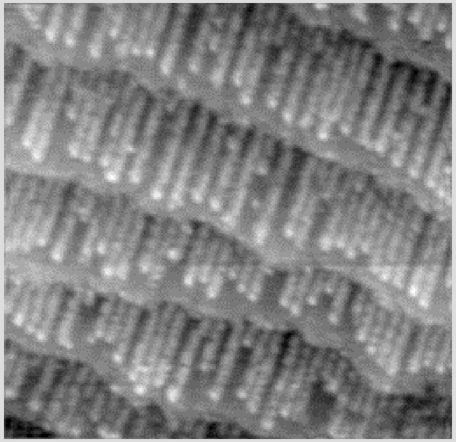
Rutile has been model surface
for many studies

Most reactions on this surface take place at defect sites



Surface Structure Influenced by Both Bulk Defects and Environment



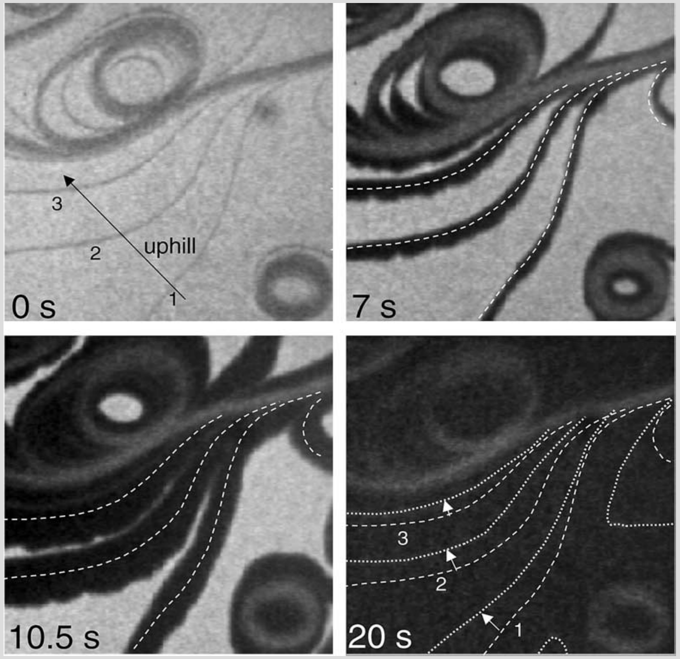


(1x1) and (1x2) surface structures on TiO_2 (110) S. Gan, Y. Liang, D.R. Baer and A. W Grant Surface Sci 475 (2001) 159-170

Spatially resolved dynamics of the $TiO_2(1\,1\,0)$ surface reconstruction

K.F. McCarty *, N.C. Bartelt

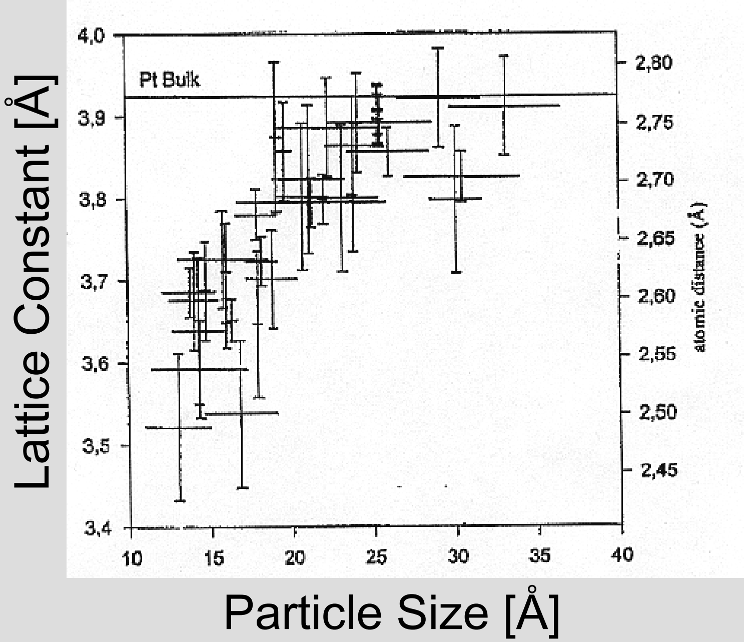
Surface Science 540 (2003) 157-171



Nanoparticles are often polymorphs of bulk material with different physical and chemical properties

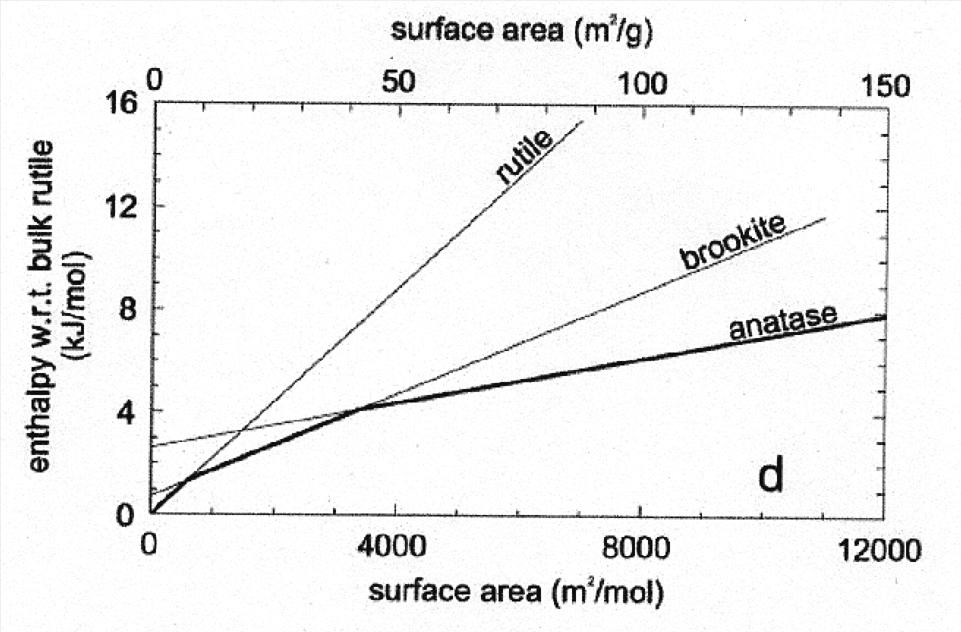
Lattice Constant for Pt as a function of cluster size

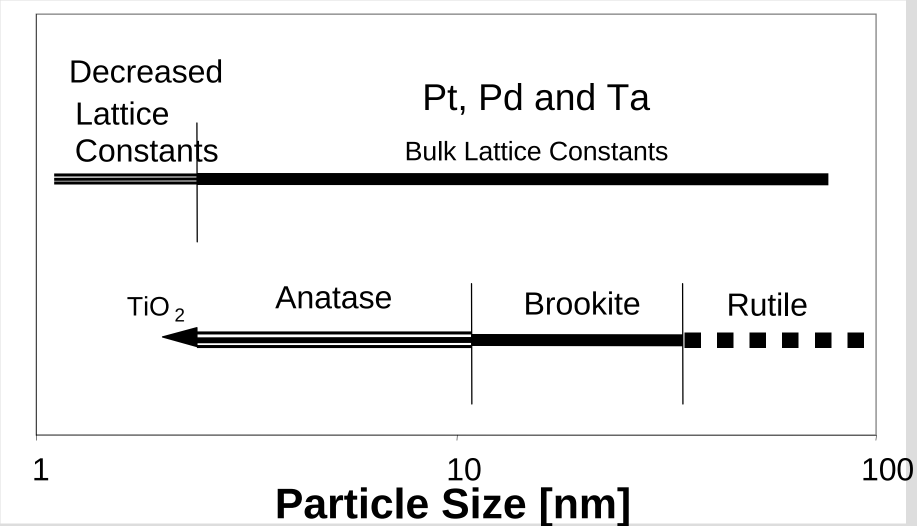
Klimenkow et al, Surf. Sci. 391 (1997) 27-36



Stable structures of TiO_2 as a function of cluster size

Ranade et al Proc. Nat. Acad. Sci. 99 (2002) 6476





Interrelationships among “bulk” structure and defects, surface structures, the environment and reactivity mean the nanoparticle properties depend on size, environment and history.

THE REACTION SPECIFICITY OF NANOPARTICLES IN SOLUTION:

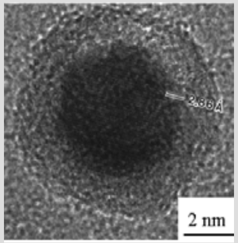
Program Components:

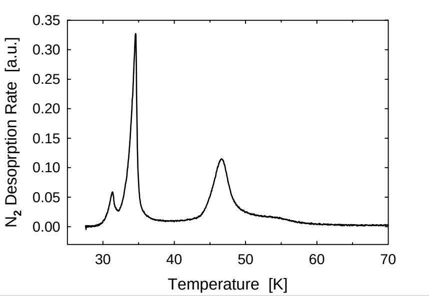
- Synthesis and characterization of Fe and Fe-Oxide nanoparticles, XPS, XAS, Mossbauer, TEM

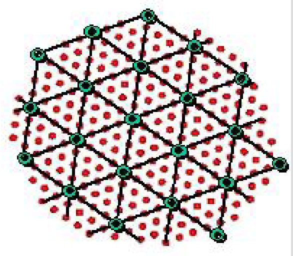
- Measurements solution and gas reactivity with Fe nanoparticles

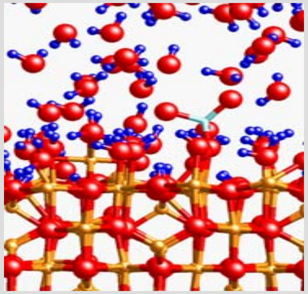
- Vacuum based studies of supported Fe nanoparticles

- Models of particle structure and effects of structure on reactivity









Summary and Concluding Thoughts

- Small particle and nanostructured materials chemistry is **relevant to** many DOE missions, including **environment**al topics

- There are **many different types of small particle** and nano-materials **effects** as well as many delightful opportunities and scientific challenges

- **More and better tools** and their use are essential to characterize the properties and environmental effects of/on nanoparticles . (Bob Hwang's multi-dimensional analysis coordinates: Space, time, energy, composition, environment)

- **Theory and modeling** are essential to successful work in this area

•Example of Size and Surface Area Effect in Atmospheric Chemistry

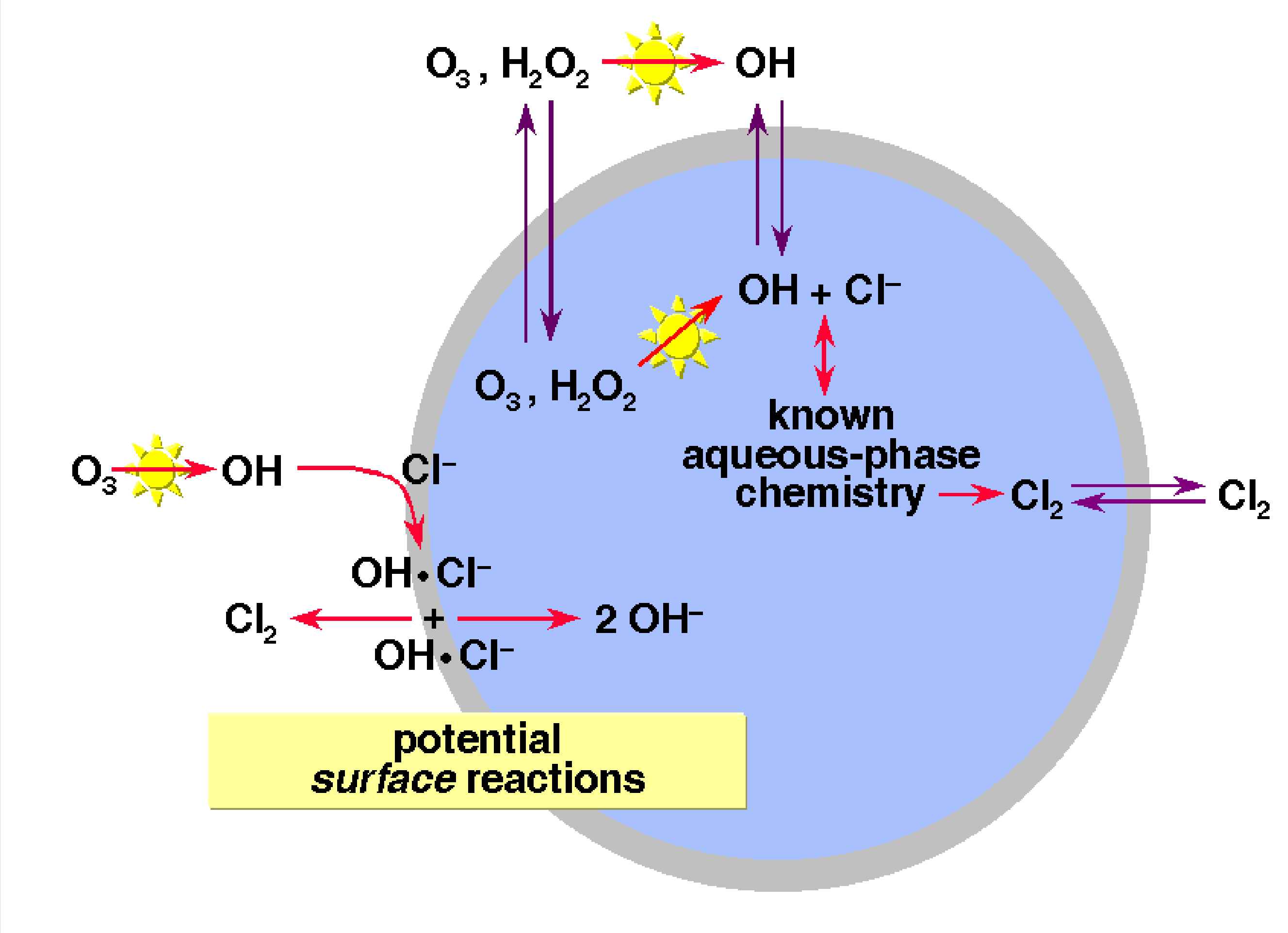
A. Laskin, D. J. Gaspar, W. Wang, S. W. Hunt, J. P Cowin, S. D. Colson, B. J. Finlayson-Pitts
Buffering Mechanism for Sea Salt Particles – Impact for Uptake of SO_2
Submitted to Science 2003

Small volume to surface area

Interface Reactions Can Raise Particle pH.

Total change depends on size of particle and time of exposure altering the environmental reactivity of small particles versus large particles

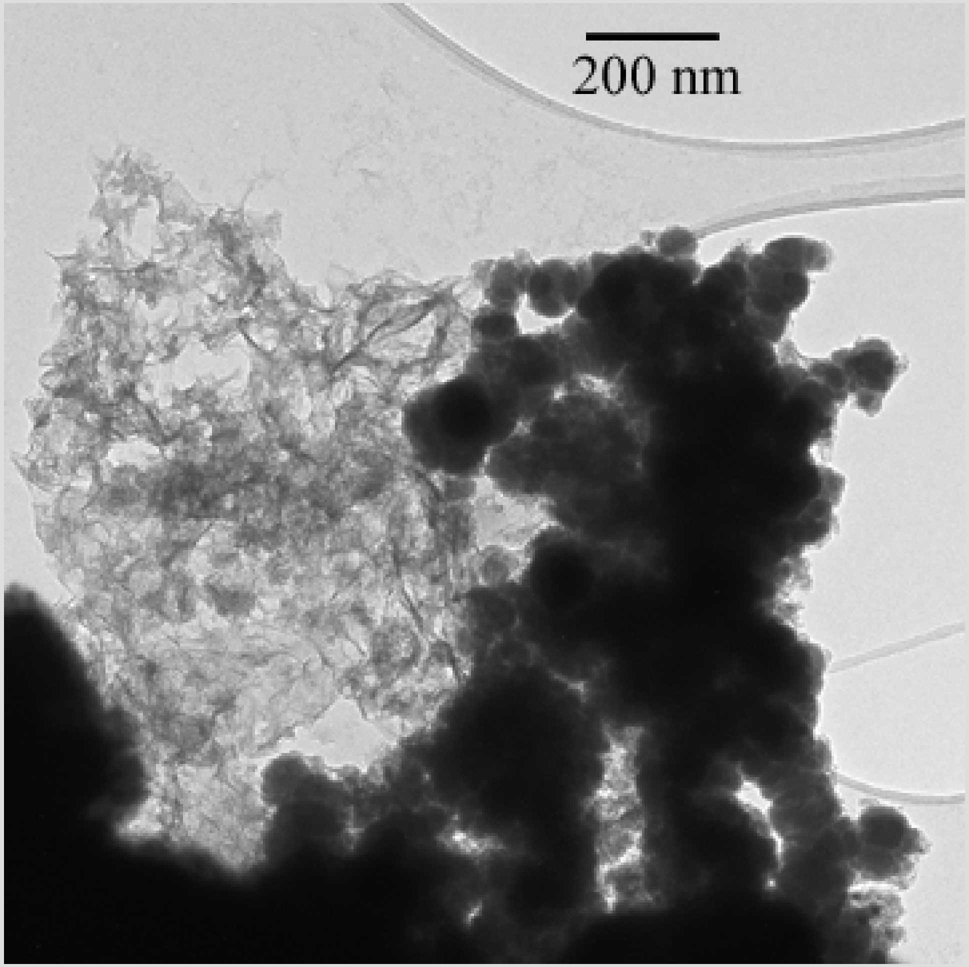
Schematic of Proposed Surface Reactions



Knipping et al., *Science* 288 301 (2000)

A. Laskin, D. J. Gaspar, W. Wang, S. W. Hunt, J. P Cowin, S. D. Colson, B. J. Finlayson-Pitts *Buffering Mechanism for Sea Salt Particles – Impact for Uptake of SO_2* Submitted to Science 2003

Zhang Sample

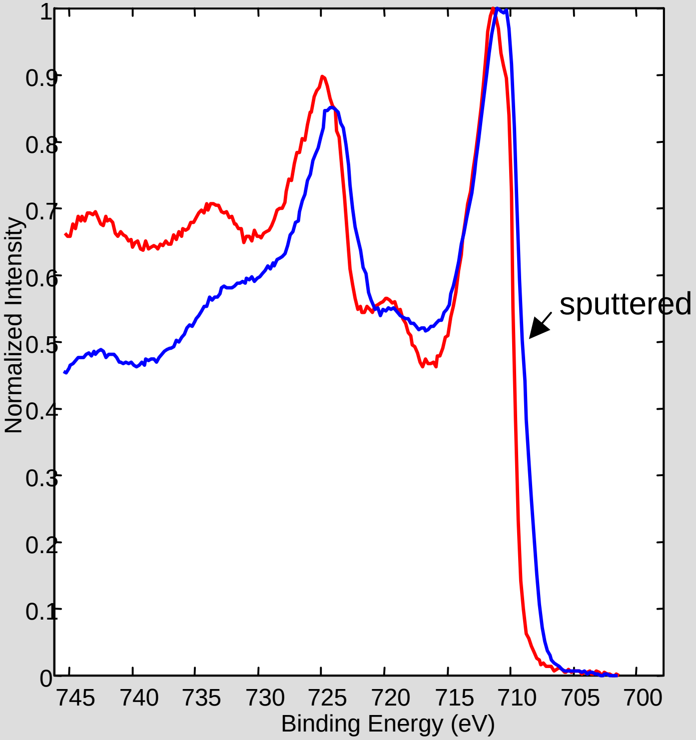


Two general types of material: flakey stuff and rounded particles that appear to have a skin of alteration

Comparison of Film and Particle Ion Beam Damage

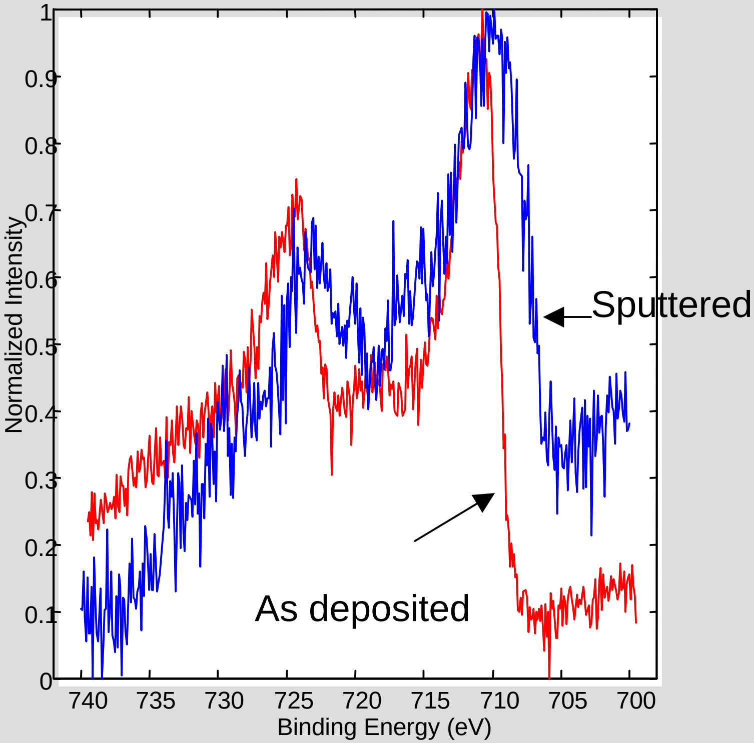
Fe_2O_3 film on Al_2O_3 as received and after 2 kV Ar^+ ion sputter (3 nm for SiO_2)

Fe 2p photoelectron peaks



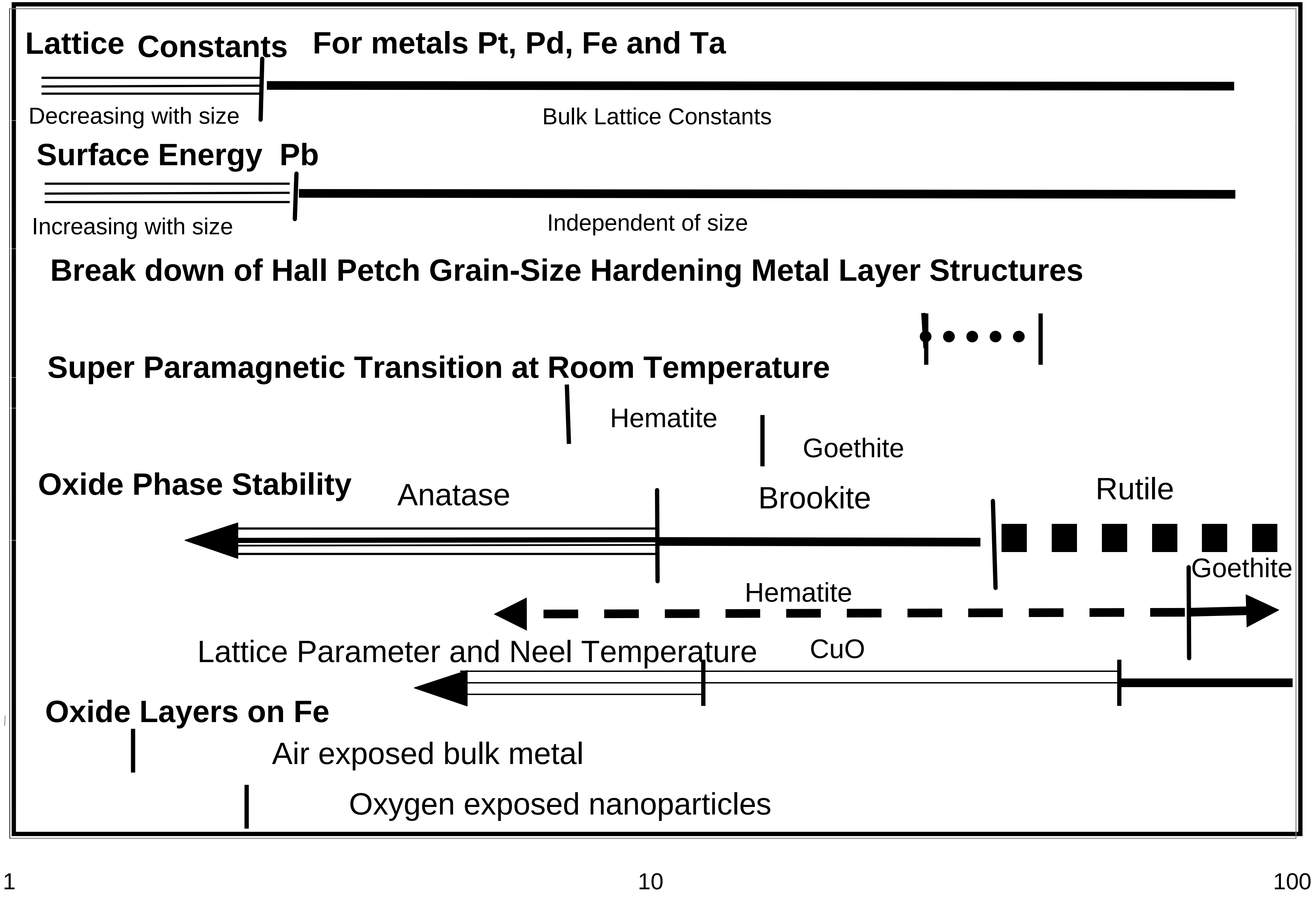
Very little selective sputtering and oxide reduction

Fe_2O_3 (?) 20 nm particles collected on Au coated Si substrate as received and after 2 kV Ar+ ion sputter (2 nm for SiO_2)



Significant reduction of particles

Characteristic Sizes for Physical and Chemical NANO Effects



Lattice Constants For metals Pt, Pd, Fe and Ta

Decreasing with size

Bulk Lattice Constants

Surface Energy Pb

Increasing with size

Independent of size

Break down of Hall Petch Grain-Size Hardening Metal Layer Structures

Super Paramagnetic Transition at Room Temperature

Hematite

Goethite

Oxide Phase Stability

Anatase

Brookite

Rutile

Goethite

Hematite

Lattice Parameter and Neel Temperature

CuO

Oxide Layers on Fe

Air exposed bulk metal

Oxygen exposed nanoparticles

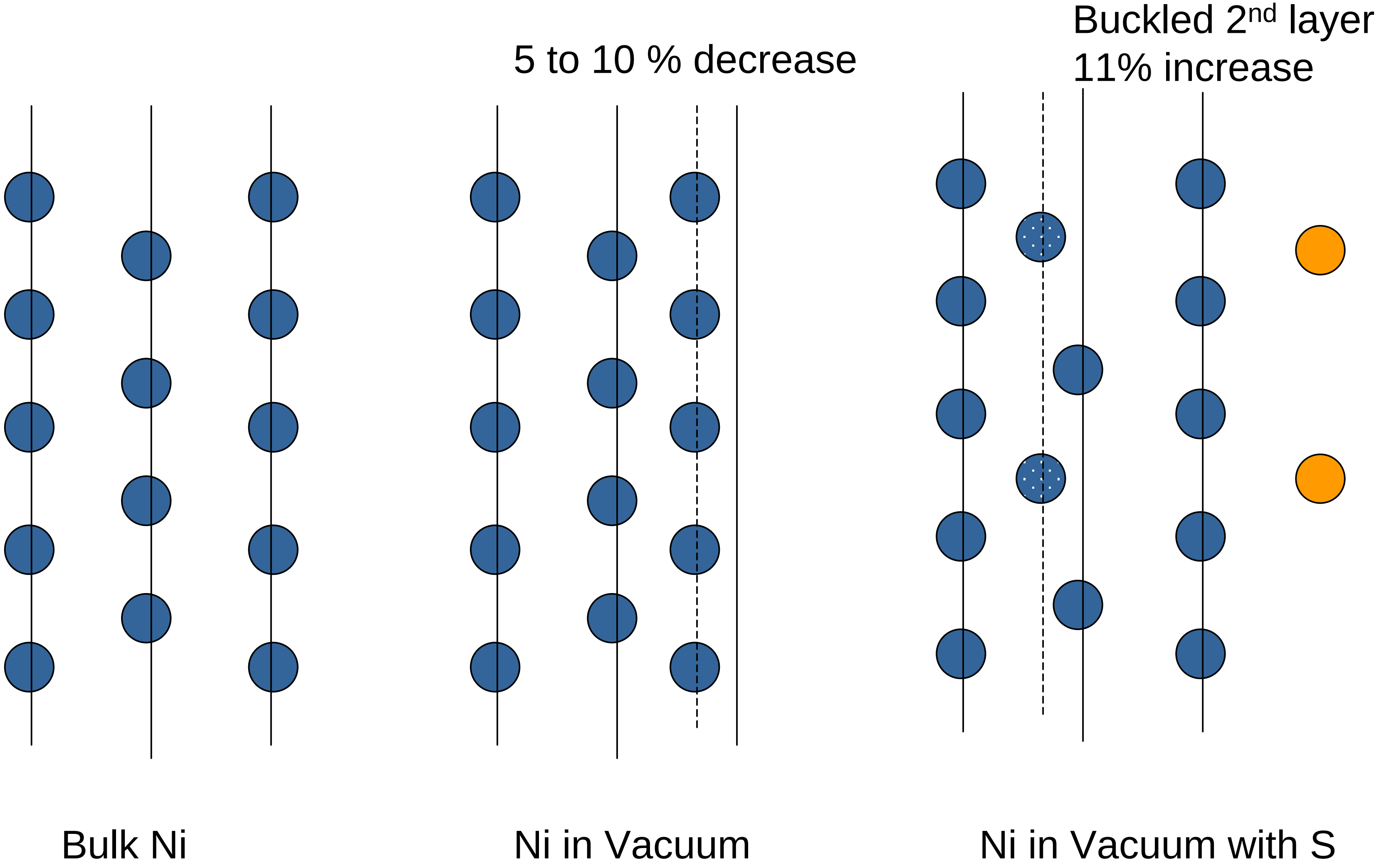
1

10

100

Critical or Characteristic Particle Sizes [nm]

Effects of Vacuum and Sulfur Sorption of Ni Surface



Even for large surfaces, vacuum and sorbates change alter structure

Danielson and Baer Corrosion Science 29 (1989) 1265-1274.