

US EPA ARCHIVE DOCUMENT



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

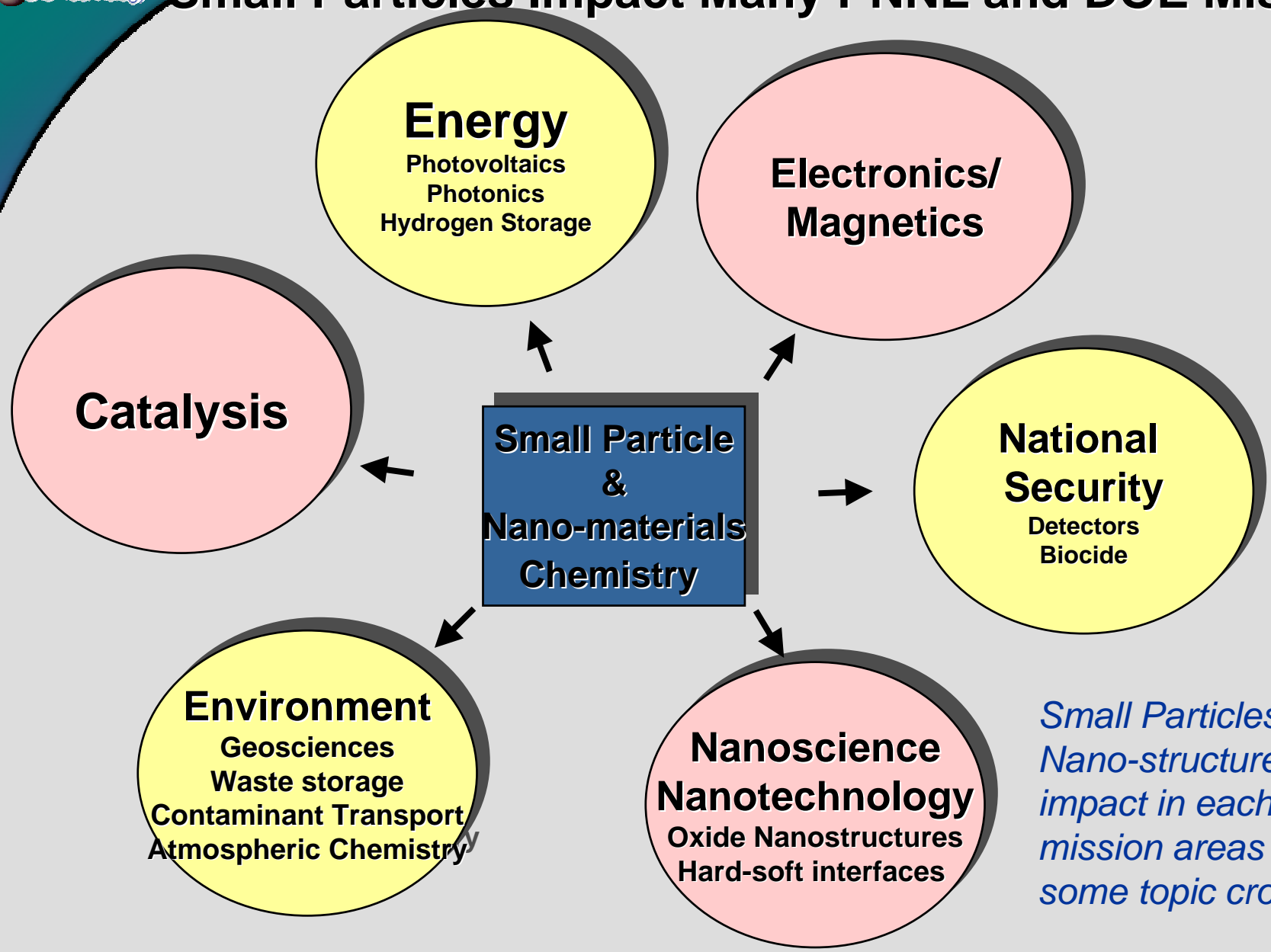
- ▶ Located in Richland, Washington
- ▶ Approximately 3,500 employees
- ▶ We deliver breakthrough science and technology to meet key national needs with a large environmental focus:

Fundamental Science  
Energy Future

Environmental Science and Technology  
National & Homeland Security



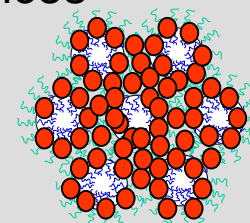
# Small Particles Impact Many PNNL and DOE Missions



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

# Nano-structured **Reactive** Materials Systems (Nano-chemistry)

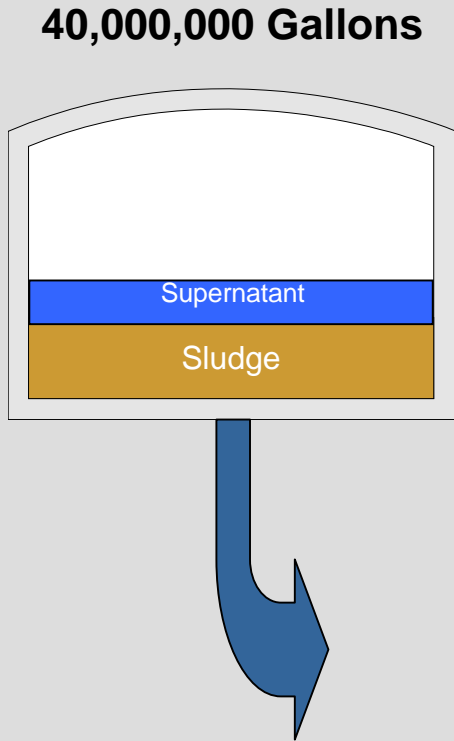
- ▶ Control of the chemical and physical properties of hierarchal materials structures containing nano-sized components to control and optimize material properties and chemical reactivity
- ▶ Application Areas
  - Catalysts for fuel cells, bioprocessing, waste reduction and the chemical industry
  - 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



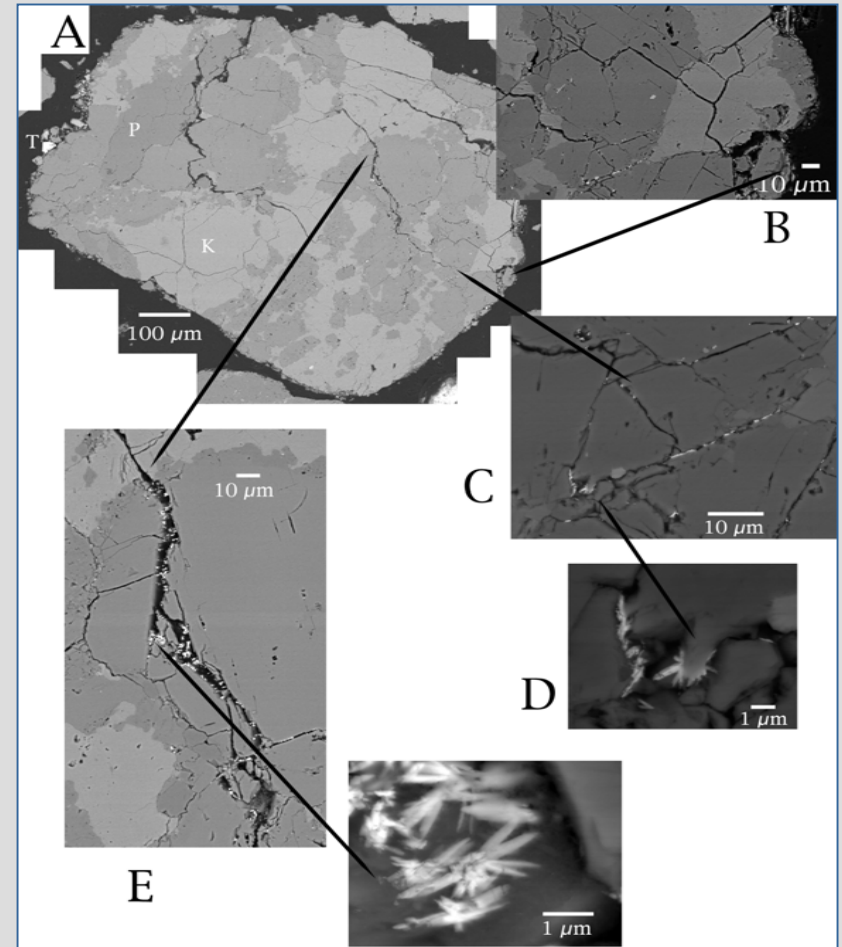


# Small Particles Important for Contaminant Transport in “Natural” System

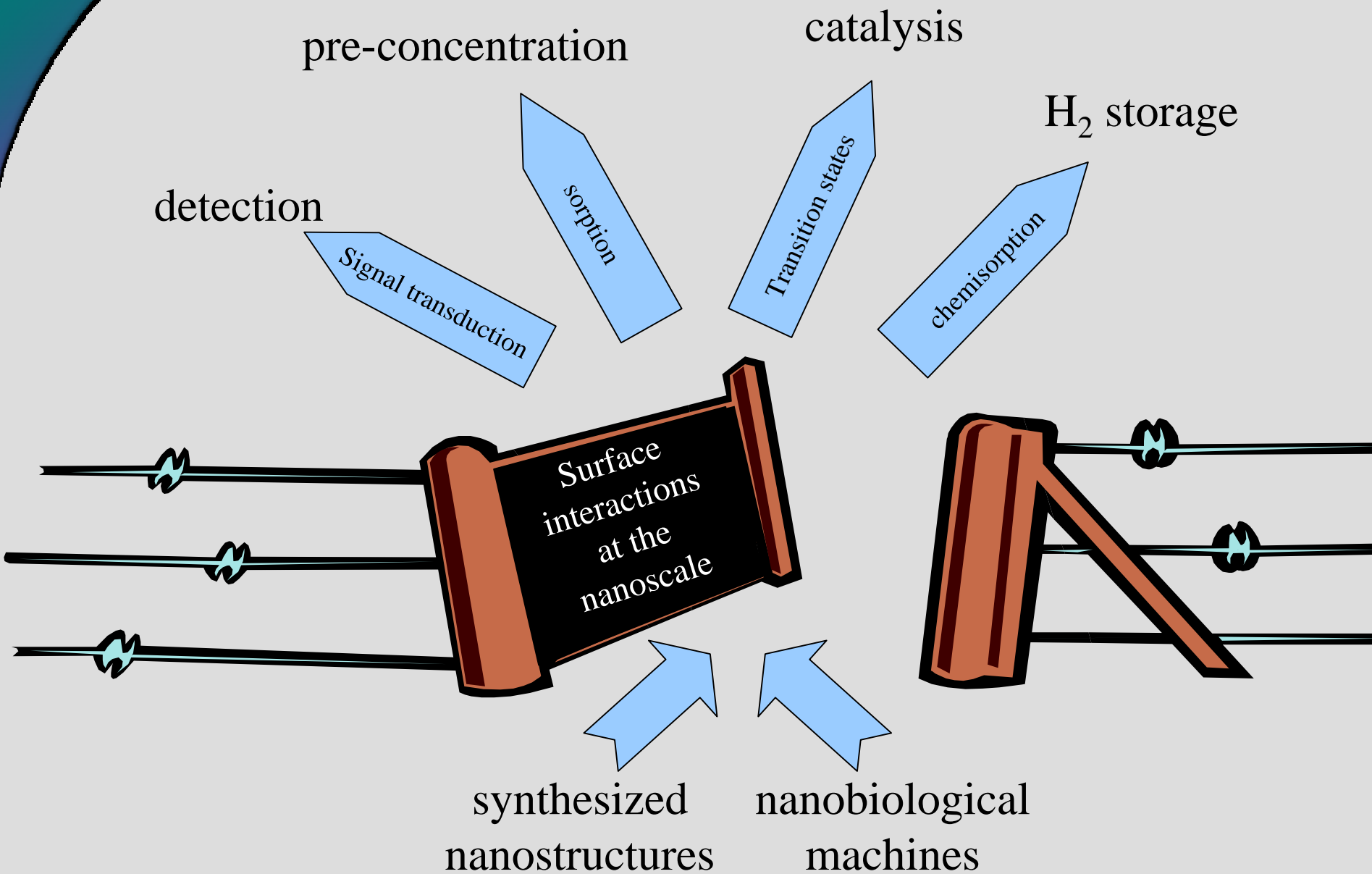
## Tank Wastes at Hanford



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



# Control of nanostructure is a gateway



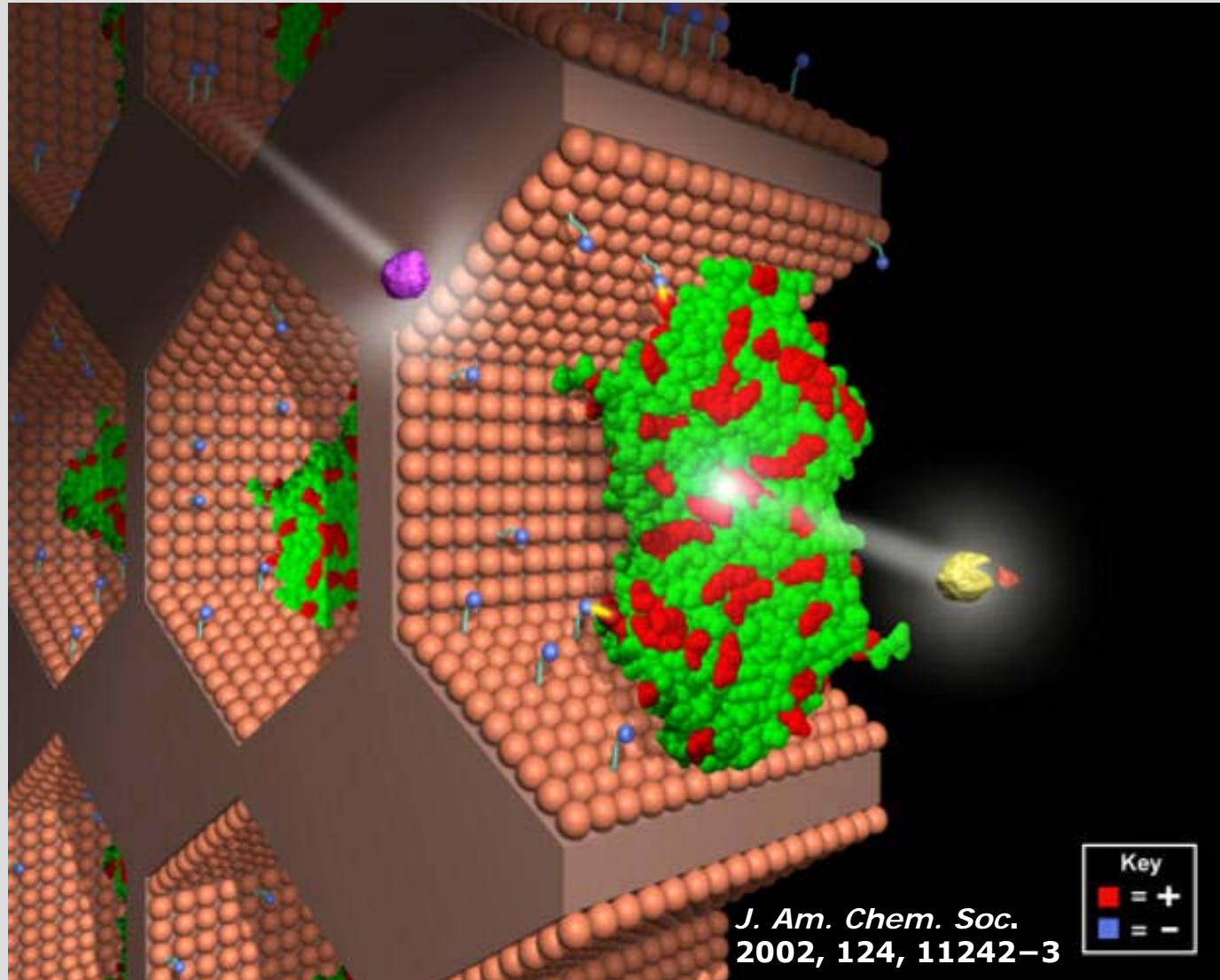


# Harnessing Enzymes: An Application of Proteins

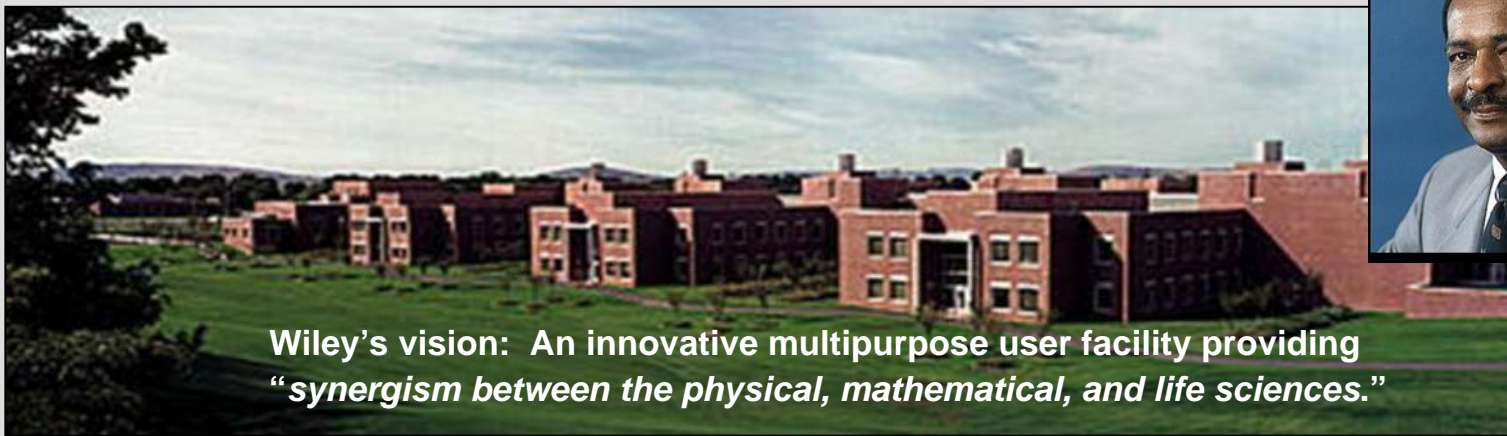
Stable enzymes entrapped in nanopores may one day be routinely used to inactivate pollutants.

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

Sensors, catalysts and separations



# Environmental Molecular Sciences Laboratory National User Facility



## ► 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

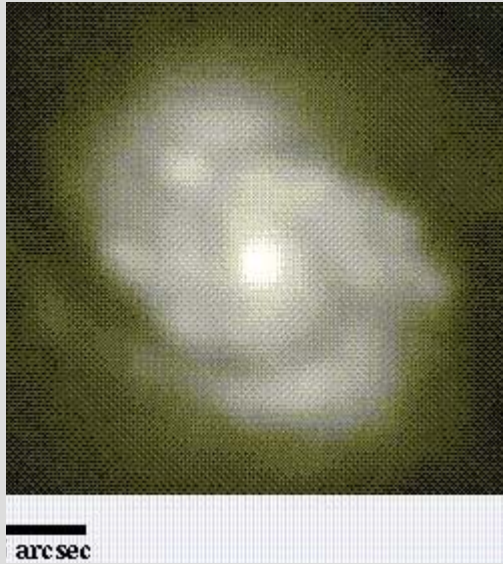
- Integration of **theory**, modeling, and simulation with **experiment**.
- **Multidisciplinary** teams and collaborative mode of operation to solve major scientific problems of interest to DOE and the nation.
- Teams who develop extraordinary **tools and methodologies**.

# 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



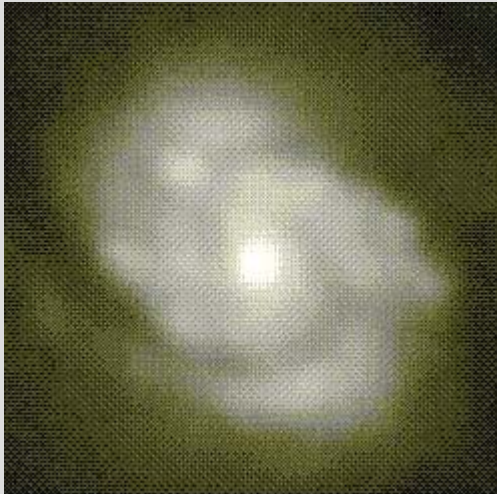
Kitt Peak  
1.1 M

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



# Calibrating the state of our understanding

Nebula M100



1 arcsec  
1 arcsec



WFPC2

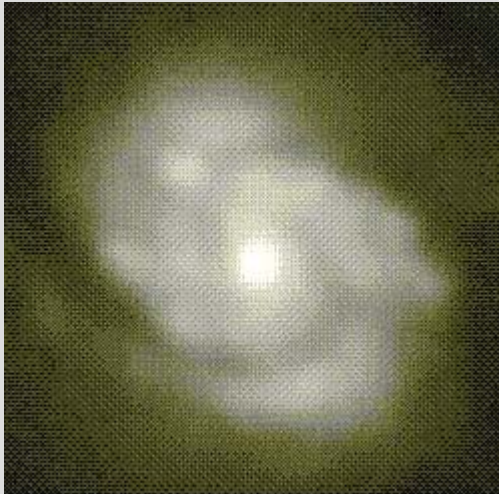
Kitt Peak  
1.1 M

Hubble  
Space  
Telescope

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

# Calibrating the state of our understanding

Nebula M100



1 arcsec  
1 arcsec

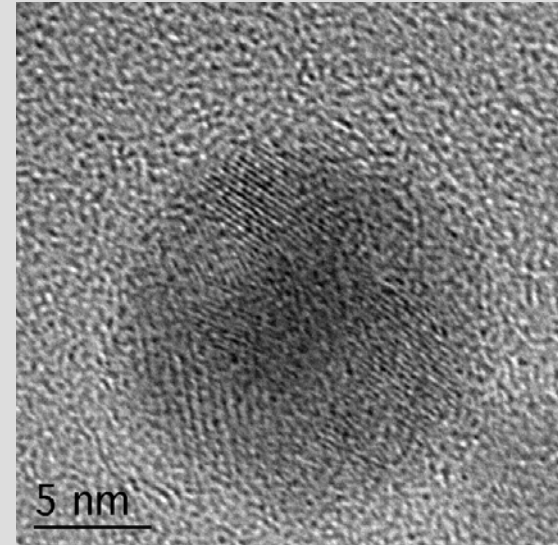
Kitt Peak  
1.1 M

Hubble  
Space  
Telescope



WFPC2

Nanoparticle Images



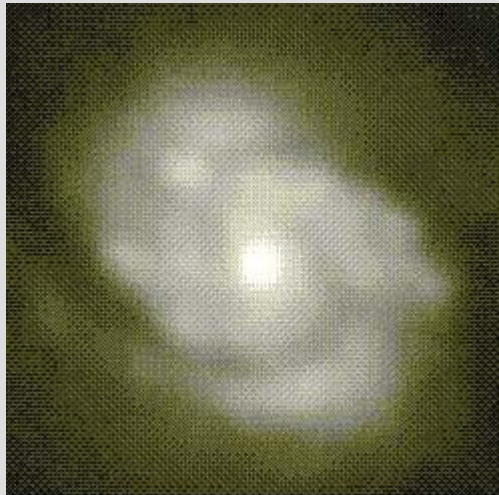
TEM of  
Fe





# Calibrating the state of our understanding

Nebula M100



arcsec  
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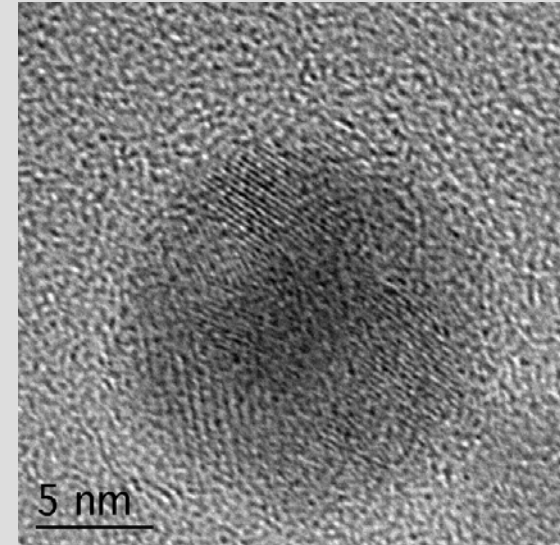
Kitt Peak  
1.1 M



WFPC2

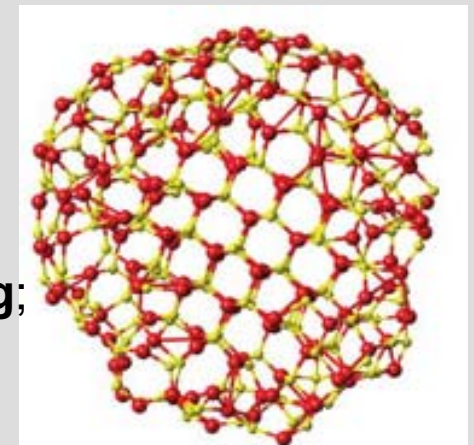
Hubble  
Space  
Telescope

Nanoparticle Images



TEM of  
Fe

Molecular Dynamics ZnS



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



# Topics

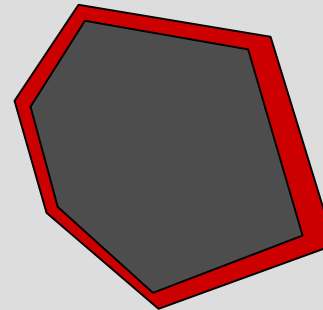
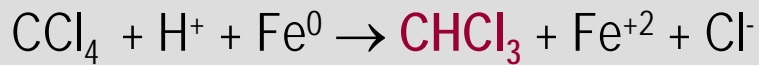
- ▶ **Chemical properties of small particle and nano-structured materials** - natural and manmade – important for PNNL Missions **most with environmental implications**
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- ▶ **Different ways that small or nano-structure makes a chemical difference.**

# THE REACTION SPECIFICITY OF NANOPARTICLES IN SOLUTION:

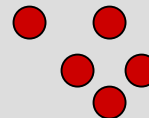
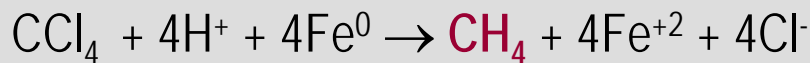
## Application to the Reaction of Nanoparticulate Iron and Iron-Bimetallic Compounds with Chlorinated Hydrocarbons and Oxyanions.

Evidence that nanoparticles change the iron induced reduction of  $\text{CCl}_4$  from **partial** reduction toward **full** removal of the Cl:

From



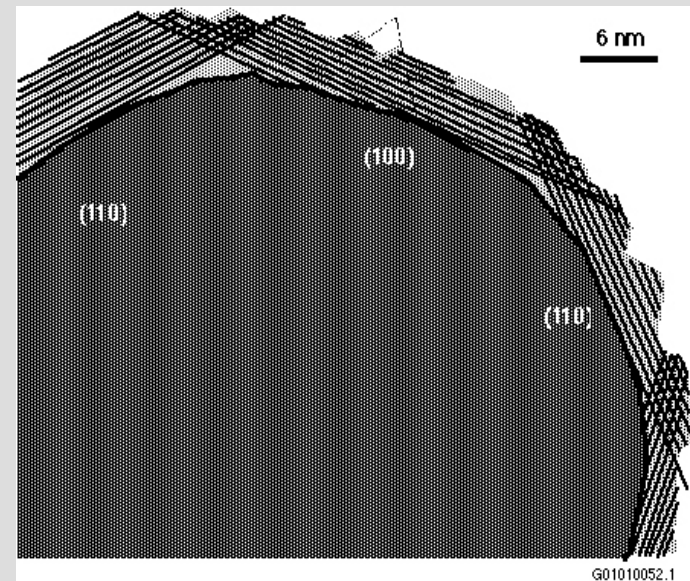
To



**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 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**

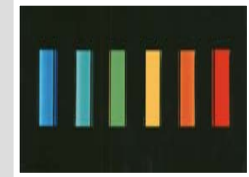
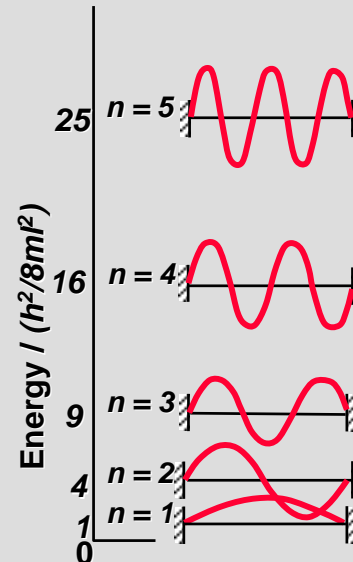
Interesting or unusual properties because the **size of the system approaches some critical length** (includes quantum effects). **Many characteristics** of material may have normal or nearly **normal** behavior

- **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



$$\text{size} \approx \zeta \approx d$$

$\zeta$  = **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

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

K= surface free energy,  $\Omega$  = 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!

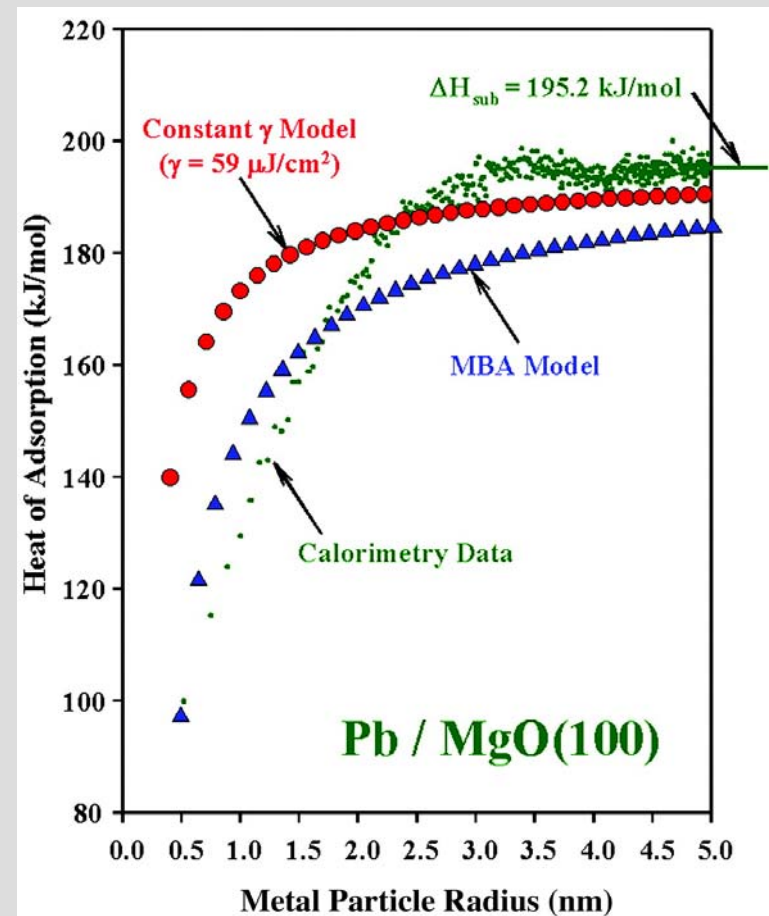
## Nanoparticle Energy 2

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**  $\approx \zeta \approx d \approx l$  (**often  $\approx$  nm**)

$\zeta$  = correlation length;  $d$  = range of intermolecular forces;  $l$  = thickness of an interface

For systems smaller than  $\zeta$  **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.**”

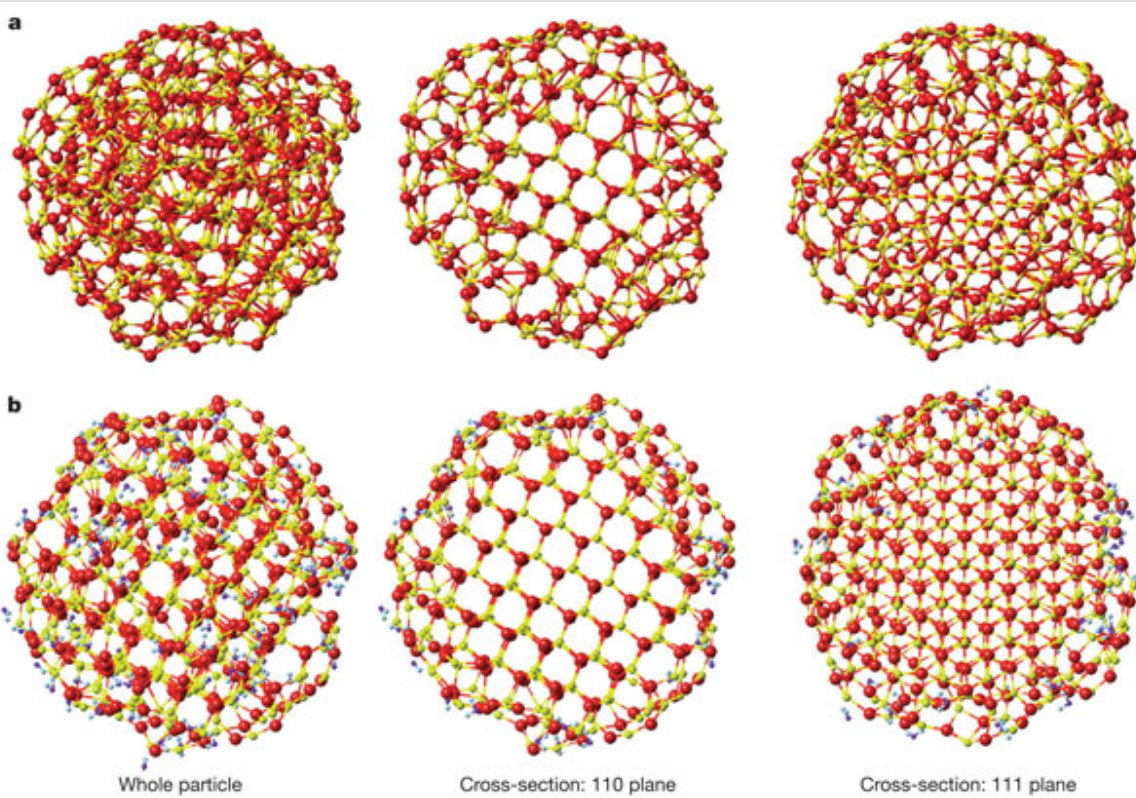


*Nature* 424, 1025 - 1029 (28 August 2003);

## **Water-driven structure transformation** in nanoparticles at room temperature

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

Vacuum



With H<sub>2</sub>O  
on surface

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

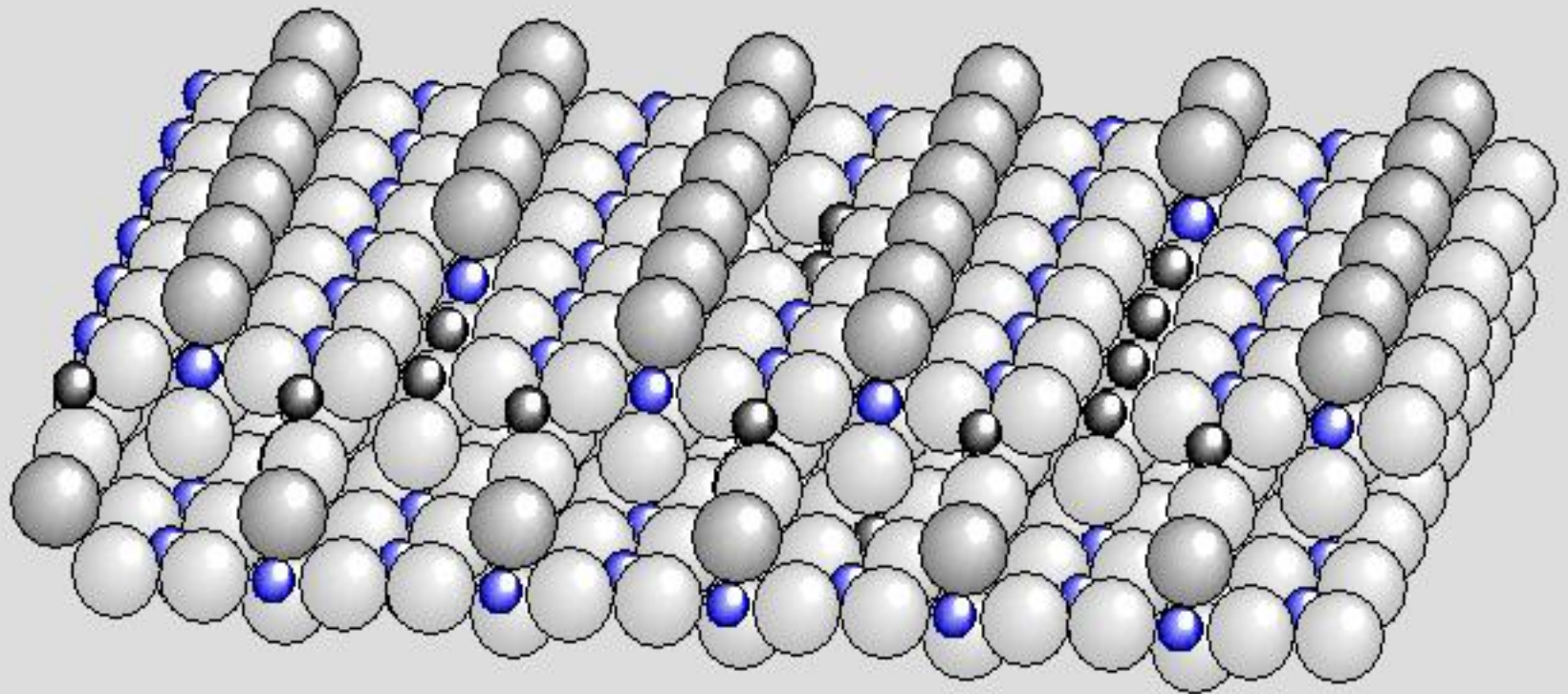
No - Consistent with theory and even experiments on “bulk” surfaces.

# Rutile $\text{TiO}_2$ [110] Surface

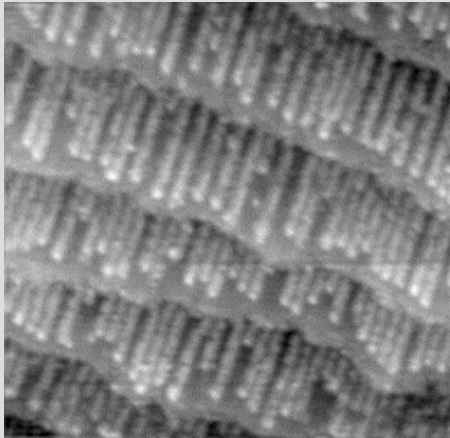
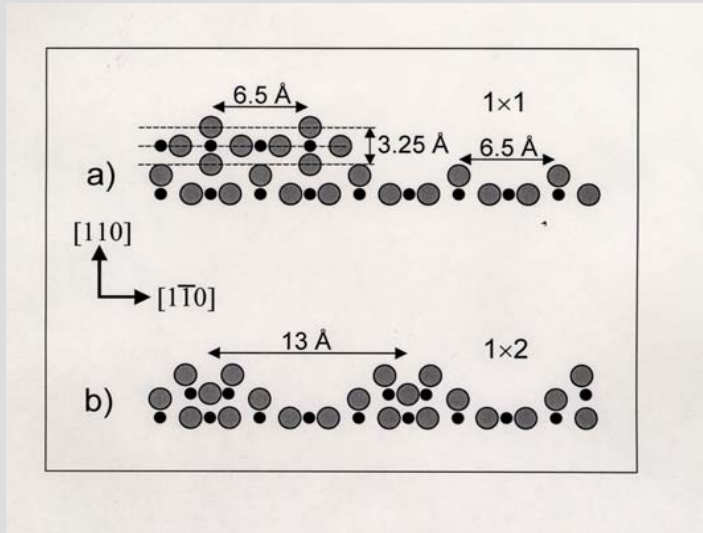
With defect sites

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

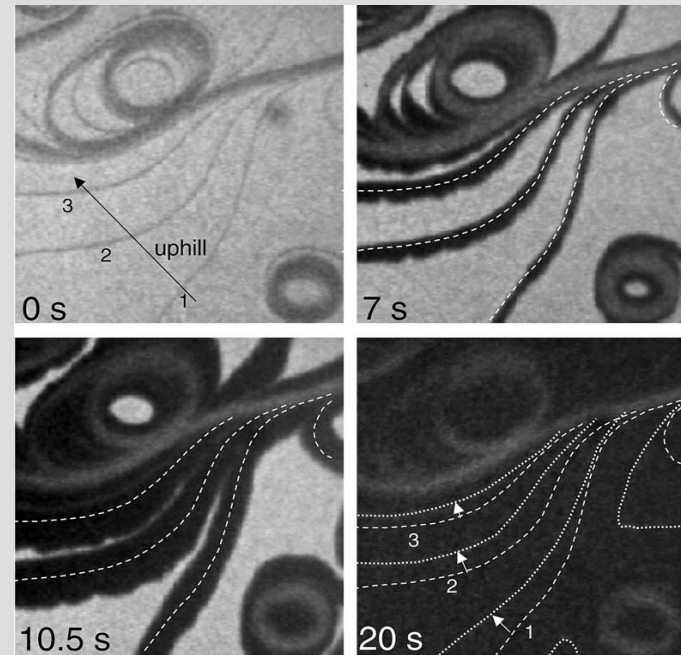


**(1x1) and (1x2) surface structures on  $\text{TiO}_2$  (110)** S. Gan, Y. Liang, D.R. Baer and A. W Grant Surface Sci 475 (2001) 159-170

## Spatially resolved dynamics of the $\text{TiO}_2(110)$ surface reconstruction

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

Surface Science 540 (2003) 157-171

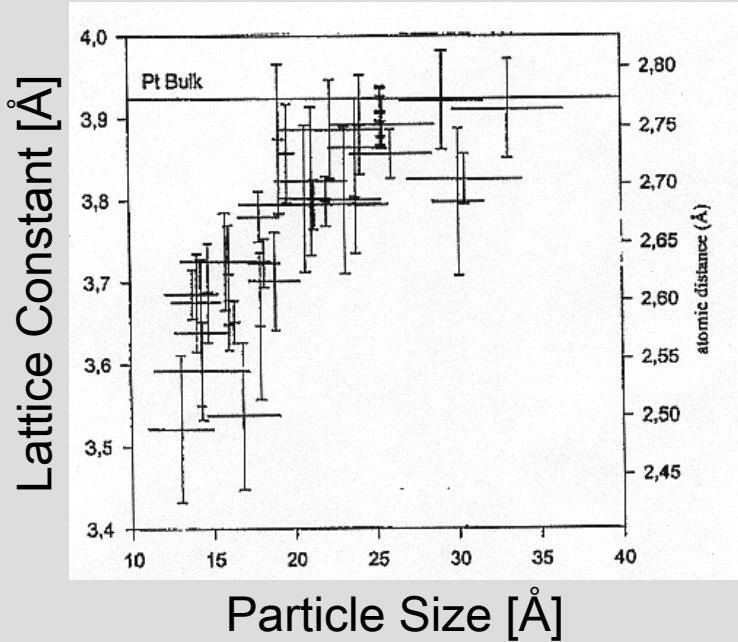




# Nanoparticles are often polymorphs of bulk material with different physical and chemical properties

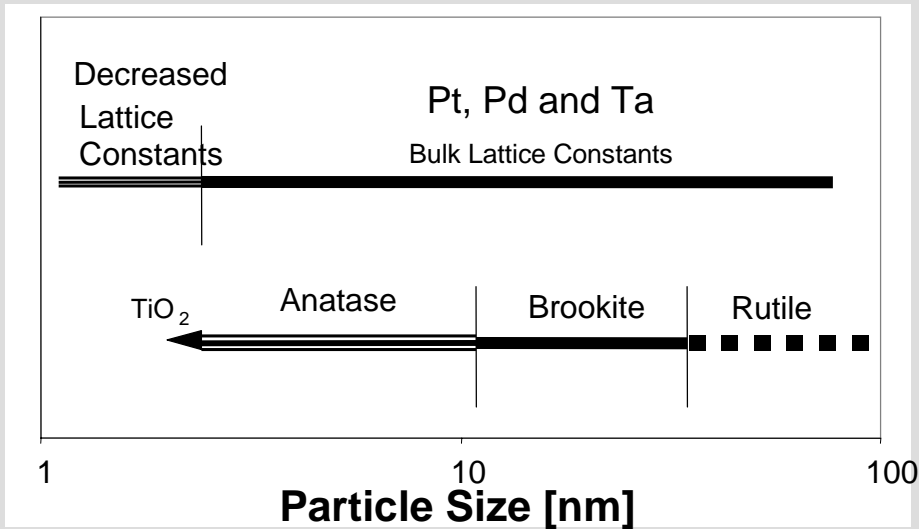
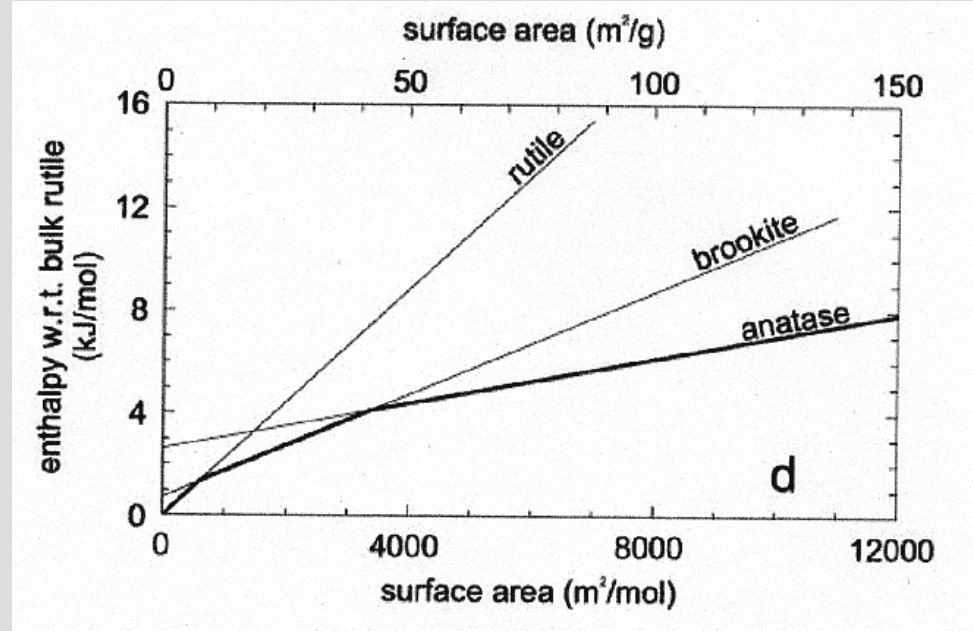
## Lattice Constant for Pt as a function of cluster size

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



## Stable structures of TiO<sub>2</sub> as a function of cluster size

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

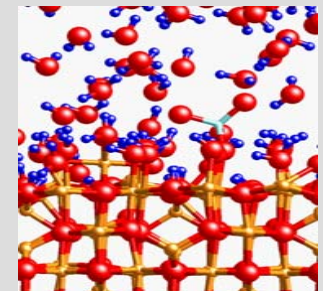
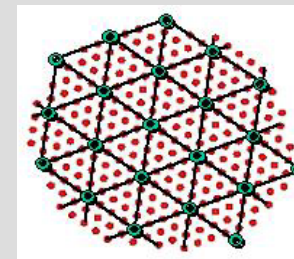
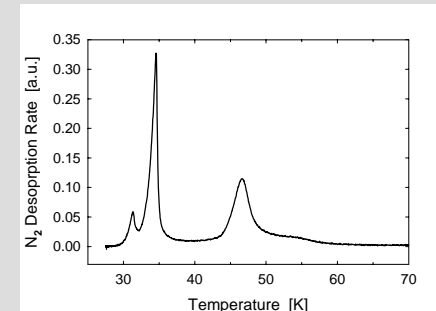
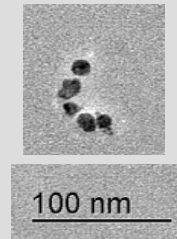
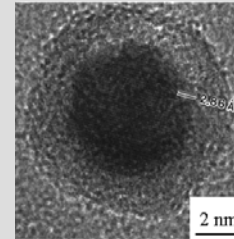


Interrelationships among “bulk” structure and defects, surface structures, the environment and reactivity mean the nanoparticle properties depend on **size**, **environment** and **history**.

# 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 **environmental** 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

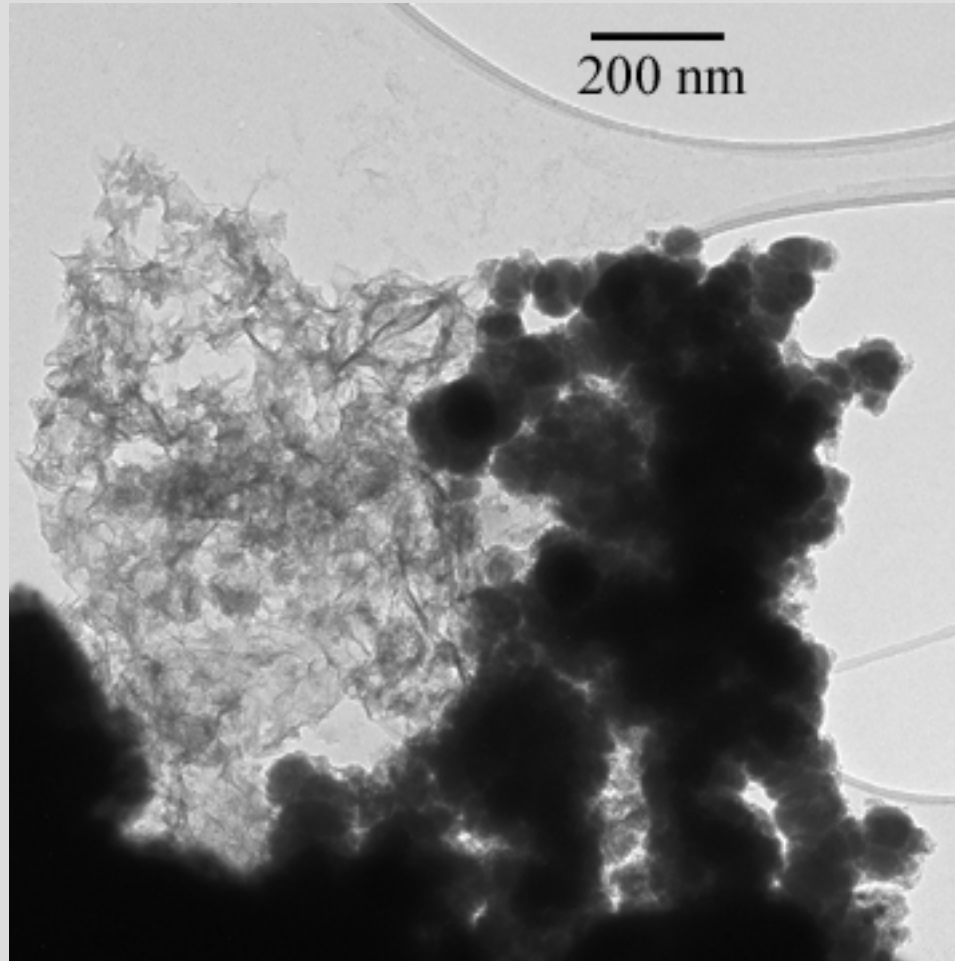
A. Laskin, D. J. Gaspar, W. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson,  
B. J. Finlayson-Pitts

*Buffering Mechanism for Sea Salt Particles – Impact for Uptake of SO<sub>2</sub>*

Submitted to Science 2003



# Zhang Sample

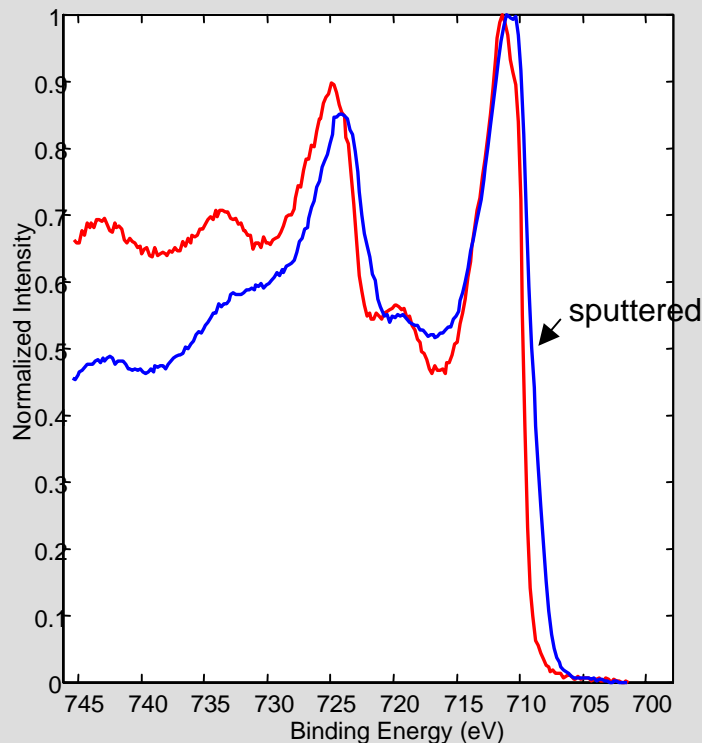


Two general types of material: flakey stuff and rounded particles that appear to have a skin of alteration

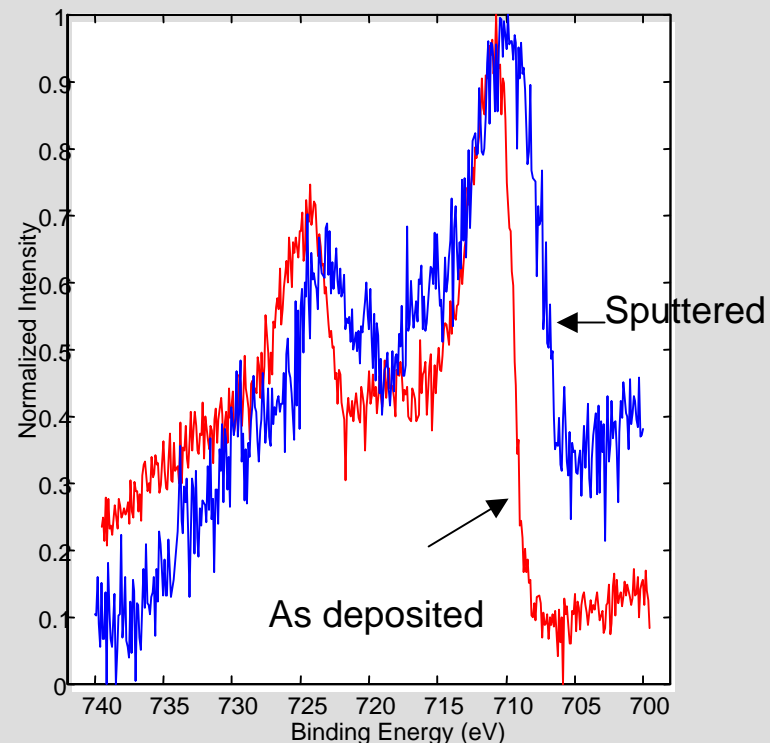
# Comparison of Film and Particle Ion Beam Damage

Fe<sub>2</sub>O<sub>3</sub> film on Al<sub>2</sub>O<sub>3</sub> as received and after 2 kV Ar<sup>+</sup> ion sputter (3 nm for SiO<sub>2</sub>)

Fe 2p photoelectron peaks



Fe<sub>2</sub>O<sub>3</sub> (?) 20 nm particles collected on Au coated Si substrate as received and after 2 kV Ar<sup>+</sup> ion sputter (2 nm for SiO<sub>2</sub>)



Very little selective sputtering and oxide reduction

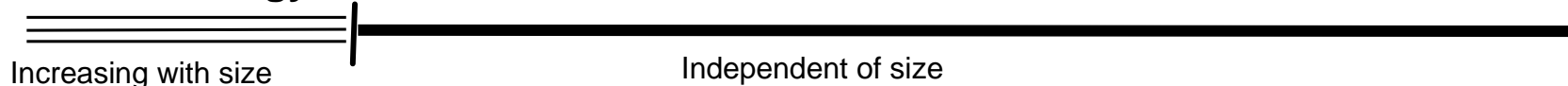
Significant reduction of particles

# Characteristic Sizes for Physical and Chemical NANO Effects

## Lattice Constants For metals Pt, Pd, Fe and Ta

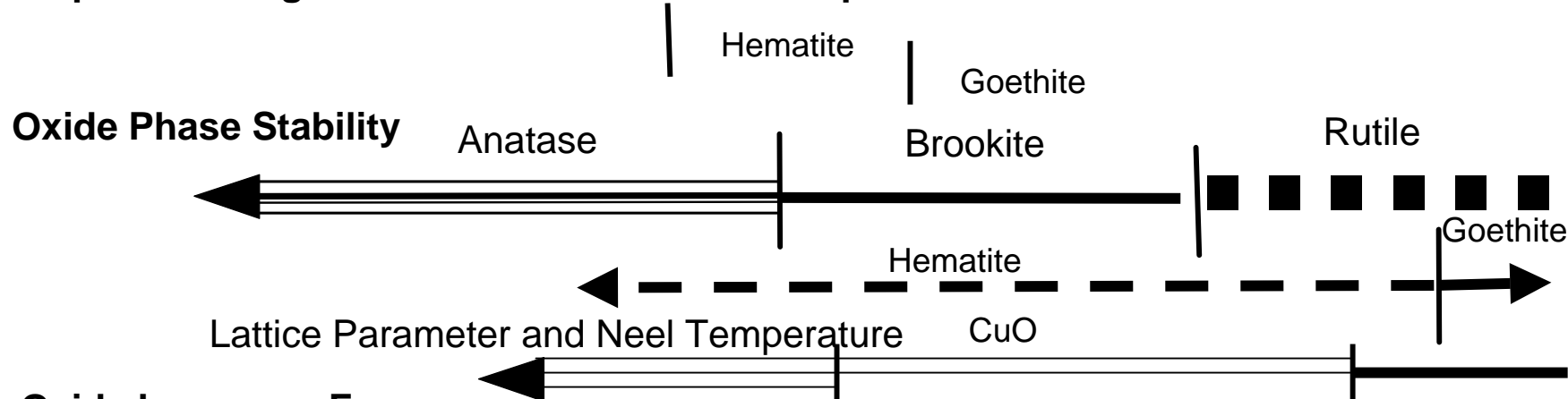


## Surface Energy Pb



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

### Super Paramagnetic Transition at Room Temperature



### Oxide Layers on Fe

Air exposed bulk metal

Oxygen exposed nanoparticles

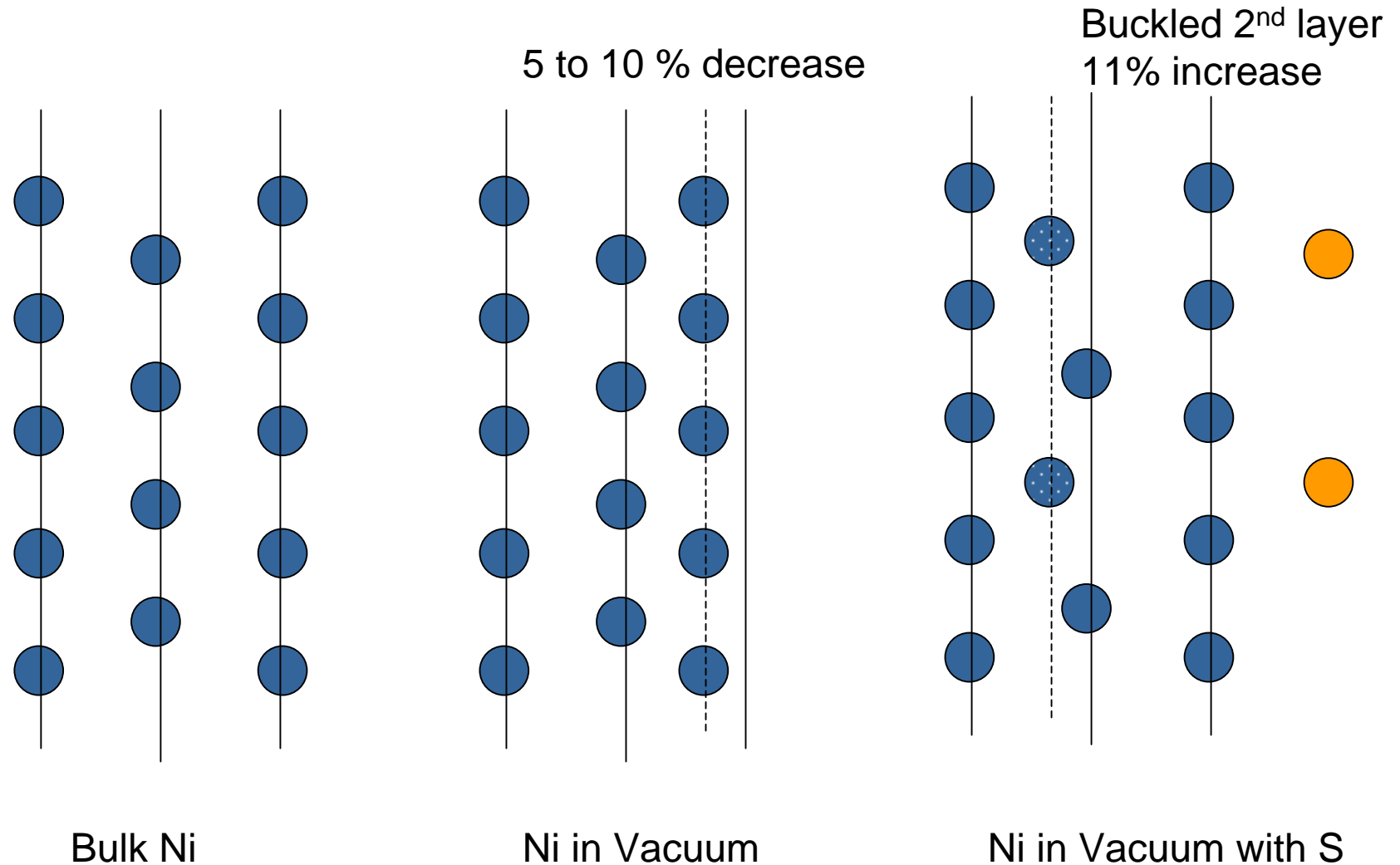
1

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.