William R. Wiley EMSL
Environmental Molecular Sciences Laboratory

Effects of the Environment and Time on Properties of Nanoparticles in Solution

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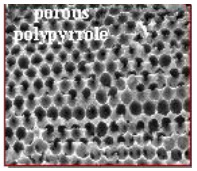
Three Different Perspectives on Understanding Nanoparticles and their role in the Environment

- Chemical, Physical and Biological properties of Ceria Nanoparticles – An EMSL User Project involving the University of Central Florida and PNNL
- Reaction Specificity of Nanoparticles in Solution - looking at chemical and physical properties of nano-particulate iron relevant to contaminant removal and cancer treatment and how they change with time (Department of Energy Research Project)
- Nanomaterials Characterization/challenges based ISO and ASTM – What do we need to do? I think there is a possible output/action from workshops such as this one.

Importance of Understanding Nano-Structured Materials

In my research and in our User Facility EMSL, we increasingly we need analyze nano-structured materials. Frequently we find that analysis of nano-structured materials involves a variety of different surprises and has more challenges than many researchers recognize.



Particle size matters: Studies fail to include basics for assessing toxicity *By Candace Stuart - Small Times Magazine 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?“**

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

Summary/Conclusions/Opinions

- Because the properties and behaviors of nanoparticles depend :
  - the environment they are in,
  - their processing history,
  - are usually time dependent,

  The properties reported by many studies will not apply more generally
- Characterization of nanoparticles is more difficult that realized by many researchers
- We are just developing some of the concepts needed to know what we really need to characterize and understand.
- Knowing the importance of time and environment should cause us to think and plan differently.

Information needed about nano-structured materials?

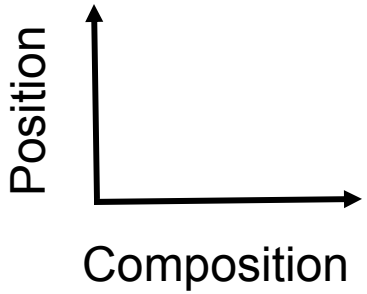
Results of Synthesis or Processing:

- size and size distribution
- composition and structure
- component segregation
- surface contamination
- defect concentration
- shape

Experimental Axes

- Energy; Composition; Spectroscopy; Structure
- Resolution; Dimension; Position

2 Dimensional Analysis



Information needed about nano-structured materials?

Results of Synthesis or Processing:

- size and size distribution
- composition and structure
- component segregation
- surface contamination
- defect concentration
- shape

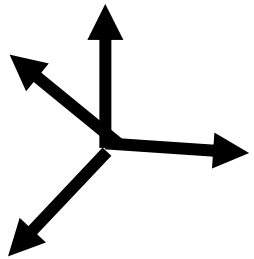
Influence of History, Aging (Time) and Environment:

- processing
- aggregation and growth
- environmental interactions
- reactive layer formation
- structure changes with time

Analyses are usually done assuming that the properties are independent of time and environment.

Experimental Axes Change to Multi Dimensional Analysis

- Energy/composition
- Resolution/Dimension
- Time
- Environment



Multi Axis Analysis from Bob Hwang BNL

Effects of Time and Environment

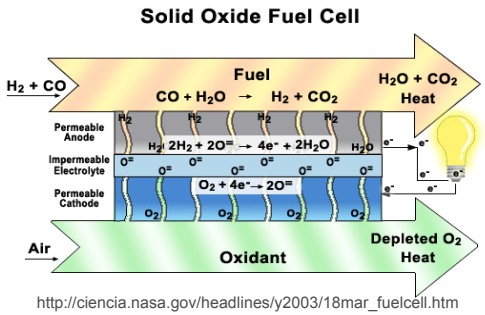
- The sensitivity of some nanoparticle properties to *time* and *environment* impacts their properties, how then can be applied, and what happens as they are accidently or deliberately placed in the environment.
- Often Ignored
- This talk looks at two specific examples of time and environmental effects:
  - Environmentally induced changes of the chemical state of **ceria nanoparticles,** impact on band gap measurements role as antioxidant in biological systems
  - Time dependent properties of **iron metal-core/oxide-shell nanoparticles** as they age and react with chlorinated hydrocarbons, and stability for medical applications.

Ceria – Nanostructured Materials

Oxygen storage properties lead to many different potential applications

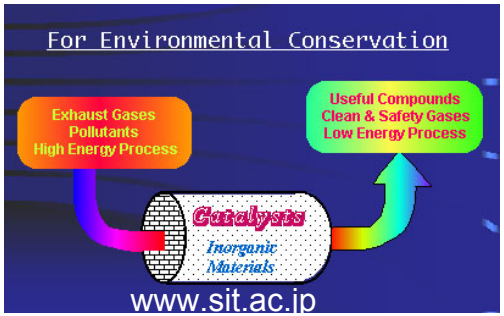
Ability to store and release oxygen an important property

Solid Oxide Fuel Cells



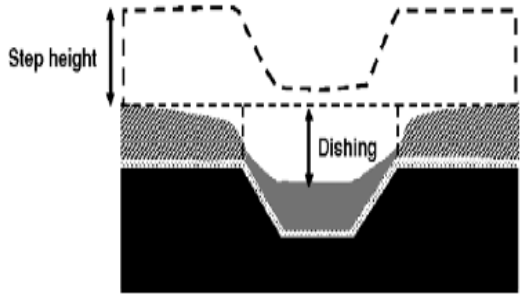
http://ciencia.nasa.gov/headlines/y2003/18mar_fuelcell.htm

Catalysis



Bio-medical Applications

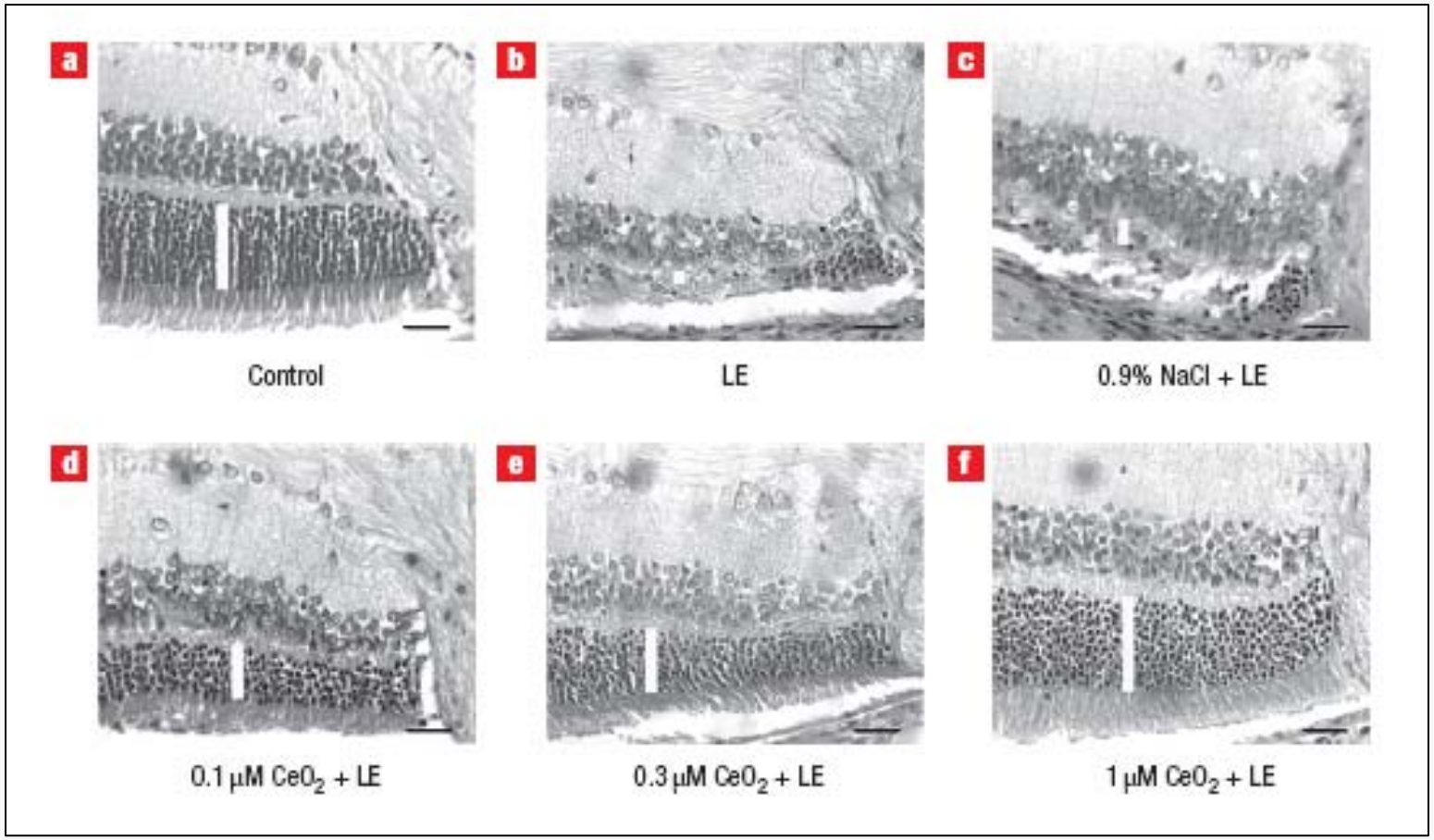
Oxidation Resistance and Anti-Reflective Coatings



Nano-Bio Ceria Applications

Protection from Light Damage

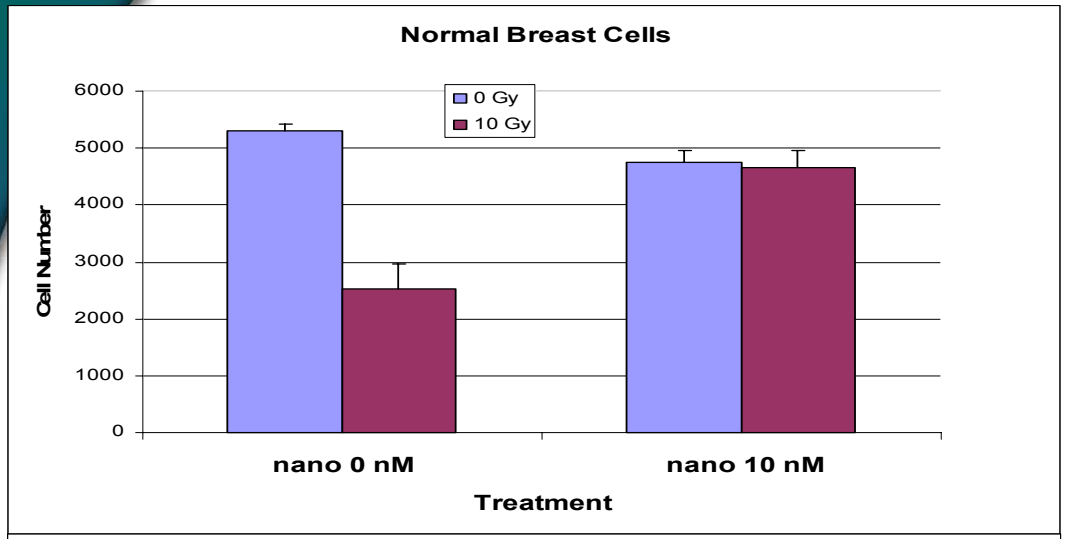
Provided by Sudipta Seal, University of Central Florida

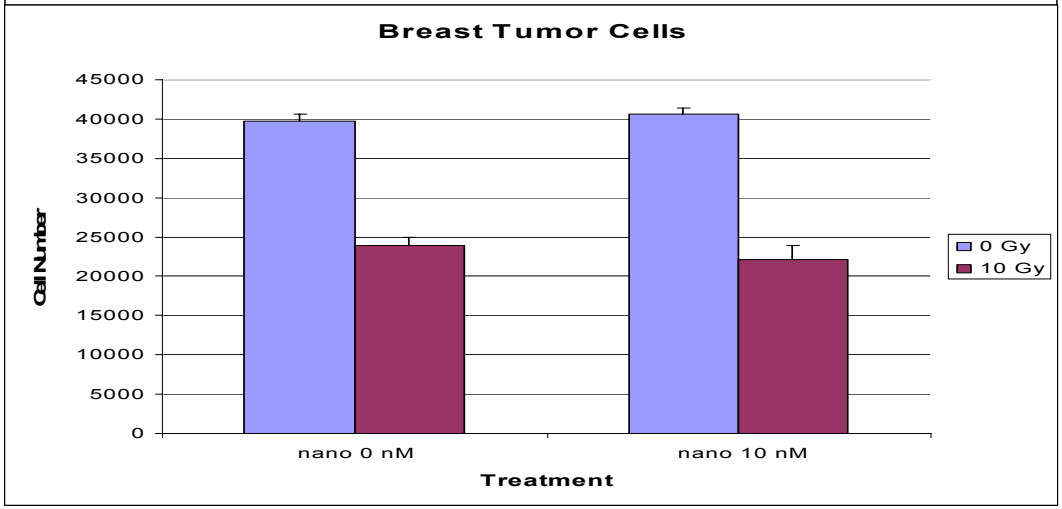


Inhibition of apoptosis by nanoparticles in rat retina subsequent to light exposure.

6 hrs, 2700 lux, repeated exposure (Neurodegenerative disease, e.g., Glaucoma) McGinnis, Seal et al., Nature Nanotechnology, 2006

Therapeutics: Radiation Therapy Cancer





- Started with 5000 normal cells.
- Started with 25000 tumor cells.
- 24 hour pre-incubation with nanoparticles at 10 nM.
- Irradiated with 10 Gy.
- Cell viability measured at 48 hours.
- See almost complete protection of normal cells.
- See no protection of tumor cells.
- Currently investigating the differential effect.
- Testing in animal model.

Seal et al., Nanoletters, 06.

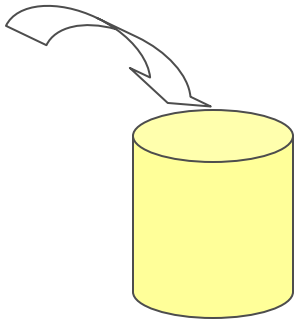
Impacts of Nano-Ceria
Uncertainties?

- Biological behavior attributed to oxygen scavenging
- Long lifetime of effect attributed to cycling between Ce^{+3} and Ce^{+4}
- Freshly made material by University of Central Florida group works well, commercial ceria nanoparticles less well
- Literature data measuring quantum confinement inconsistent or contradictary

Formation of Ceria Nanoparticles

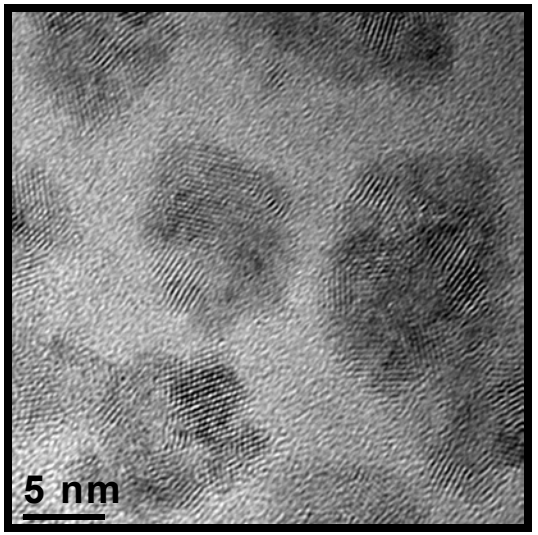
$Ce^{3+} + OH^- + ½ H_2O_2 \rightarrow Ce(OH)_2^{2+}$

$Ce(OH)_2^{2+} + 2 OH^- \rightarrow Ce(OH)_4 \rightarrow CeO_2.2H_2O$

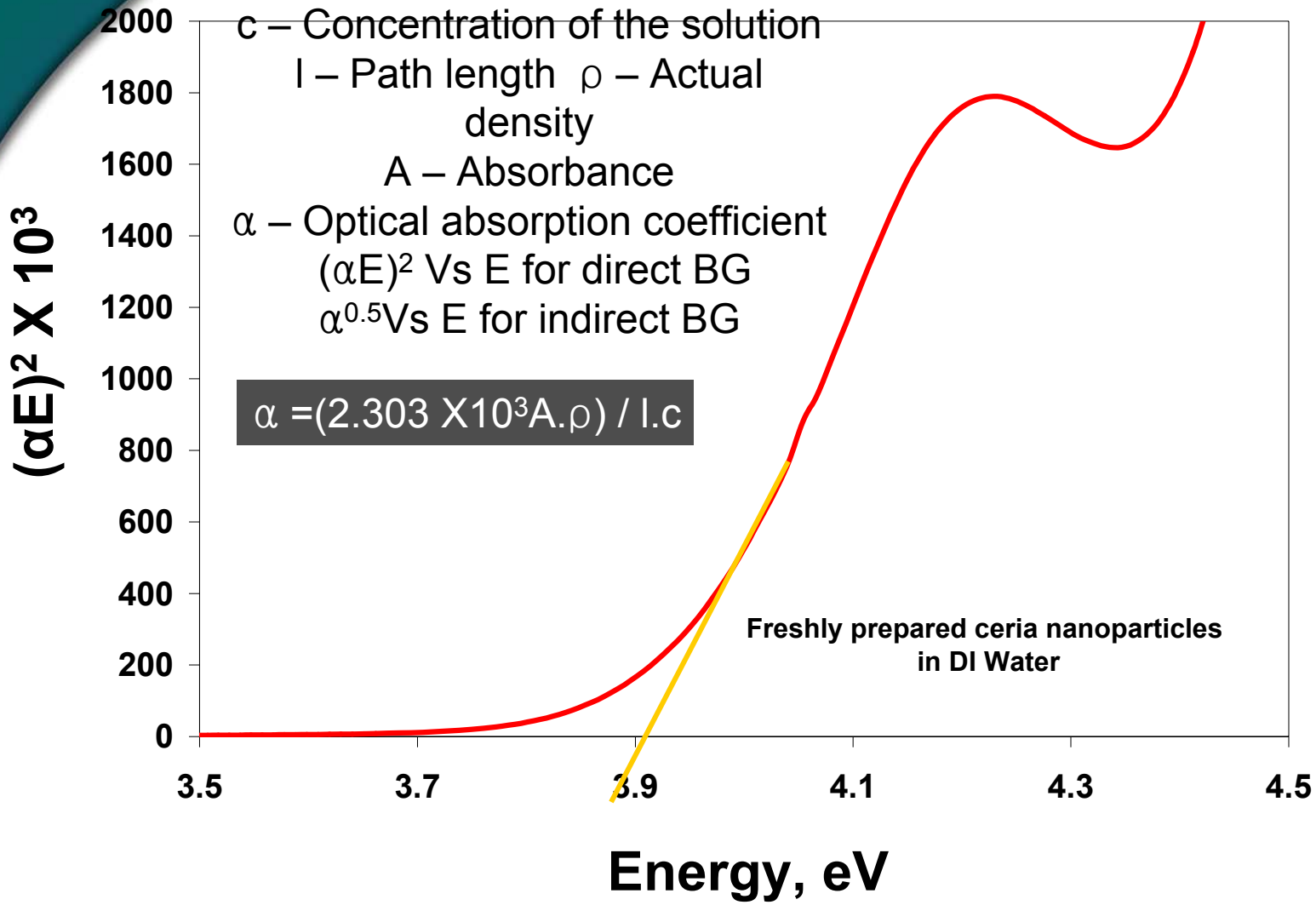


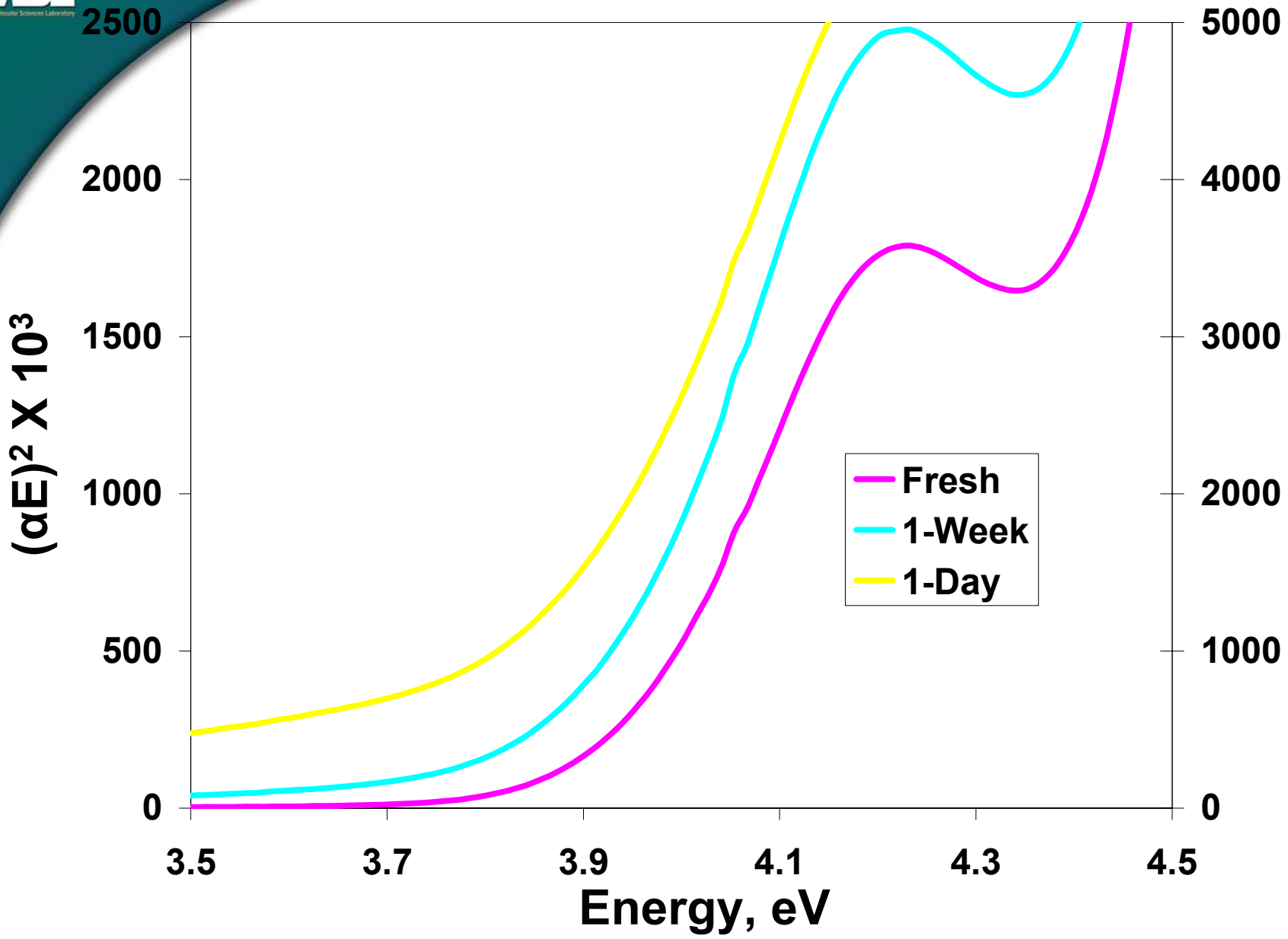
Particles form quickly when peroxide added salt solution

TEM of particles harvested within an hour show 3-5 nm particles in 15-20 nm agglomerates. Particles appear the same to TEM analysis for all conditions to follow

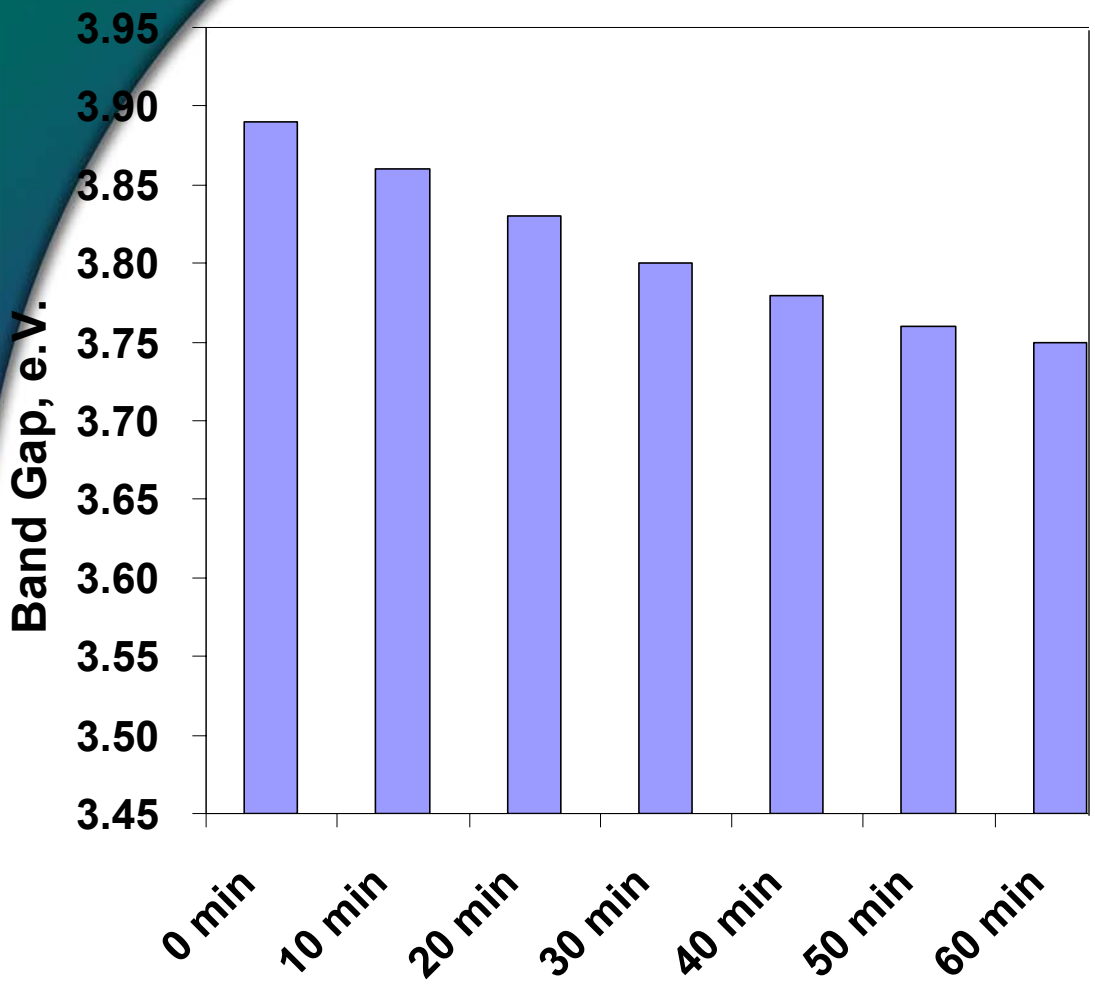


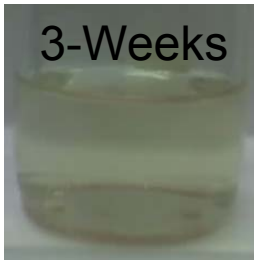
- 15-20nm agglomerates
- No specific morphology


c – Concentration of the solution
l – Path length ρ – Actual density
A – Absorbance
α – Optical absorption coefficient
(αE)2 Vs E for direct BG
α0.5Vs E for indirect BG
α =(2.303 X10³A.ρ) / l.c
Freshly prepared ceria nanoparticles in DI Water
(αE)² X 10³
2000
1800
1600
1400
1200
1000
800
600
400
200
0
3.5
3.7
3.9
4.1
4.3
4.5
Energy, eV


2500
2000
1500
1000
500
0
5000
4000
3000
2000
1000
0
(αE)² X 10³
3.5
3.7
3.9
4.1
4.3
4.5
Energy, eV
Fresh
1-Week
1-Day

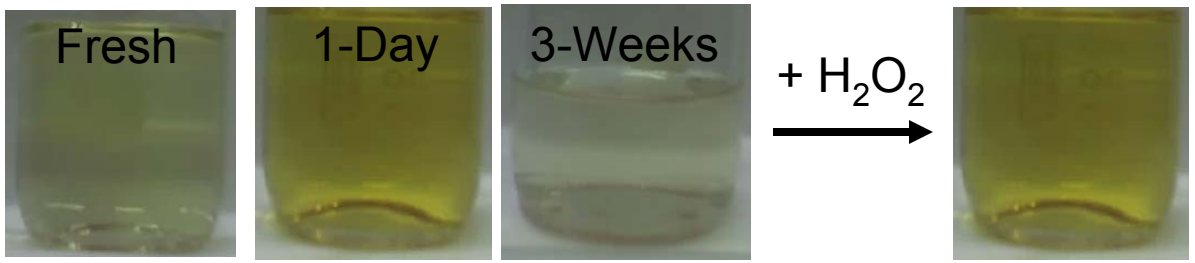
Bohr radius ~7.0nm

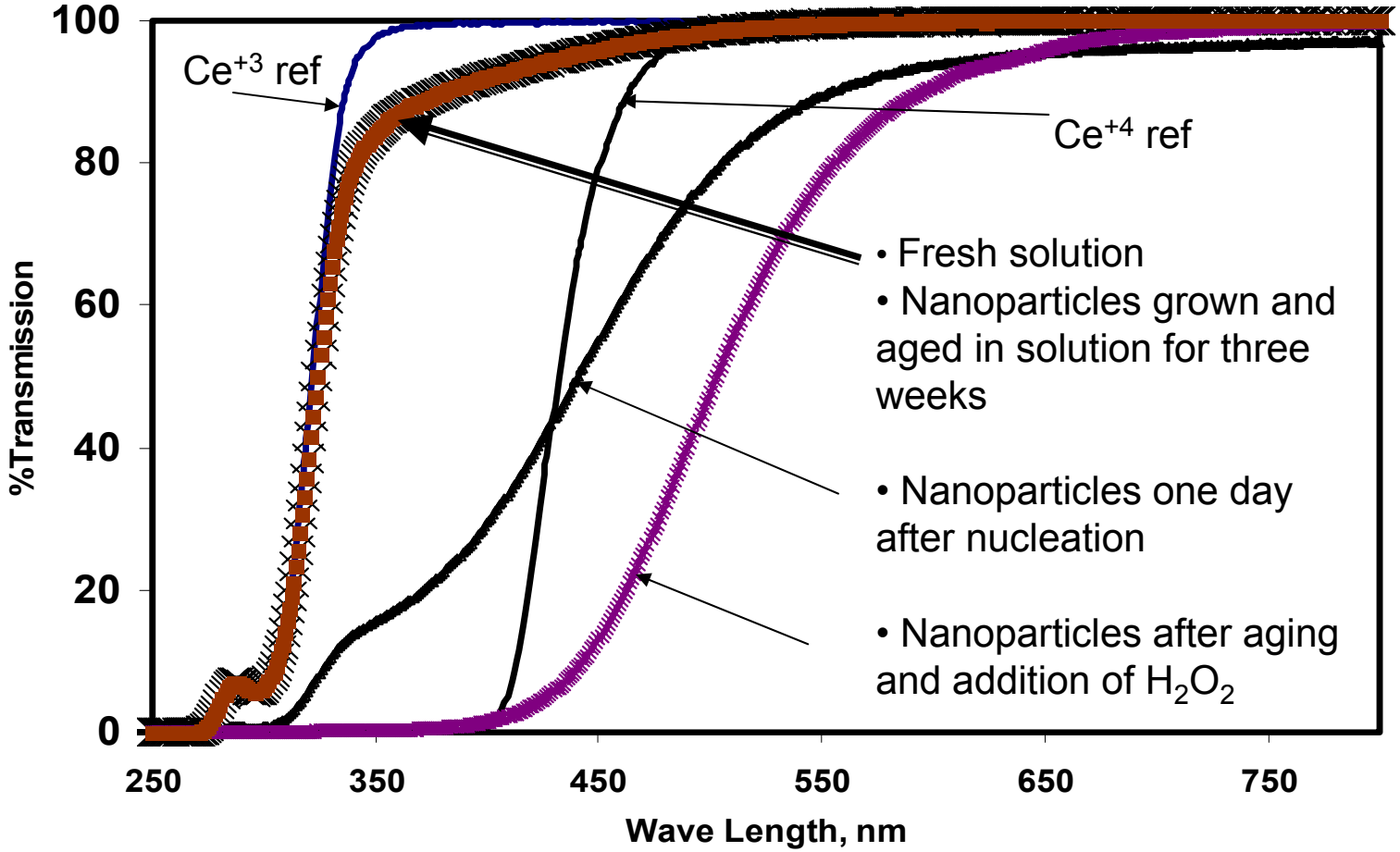


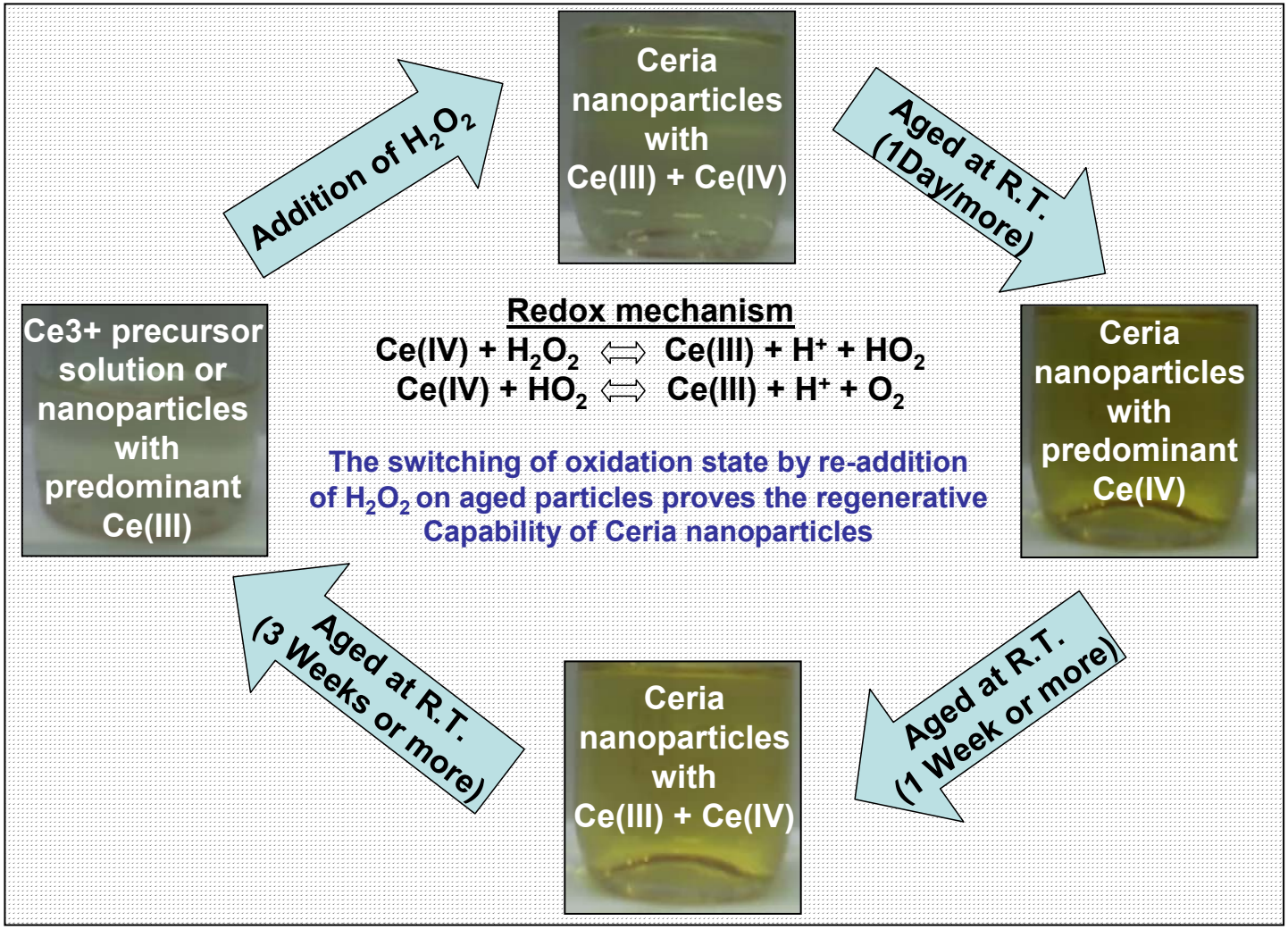


Band gap variation in water based ceria nanoparticles as a function of time

UV – Visible Transmission
Nanoparticles at different times and reference salts





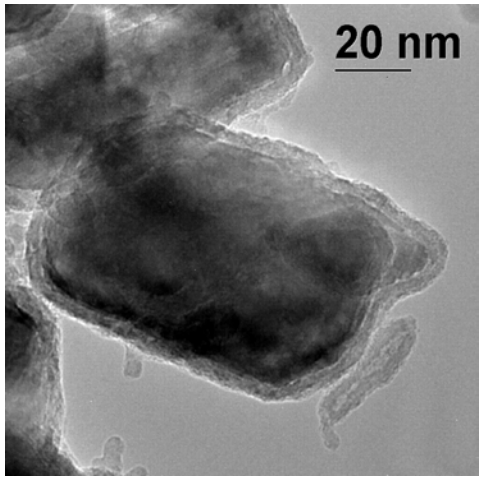

Ceria nanoparticles with Ce(III) + Ce(IV)
Addition of H_2O_2
Aged at R.T. (1Day/more)
Ce3+ precursor solution or nanoparticles with predominant Ce(III)
Redox mechanism
$Ce(IV) + H_2O_2 \Leftrightarrow Ce(III) + H^+ + HO_2$
$Ce(IV) + HO_2 \Leftrightarrow Ce(III) + H^+ + O_2$
The switching of oxidation state by re-addition of H_2O_2 on aged particles proves the regenerative Capability of Ceria nanoparticles
Ceria nanoparticles with predominant Ce(IV)
Aged at R.T. (3 Weeks or more)
Ceria nanoparticles with Ce(III) + Ce(IV)
Aged at R.T. (1 Week or more)

Summary Ceria

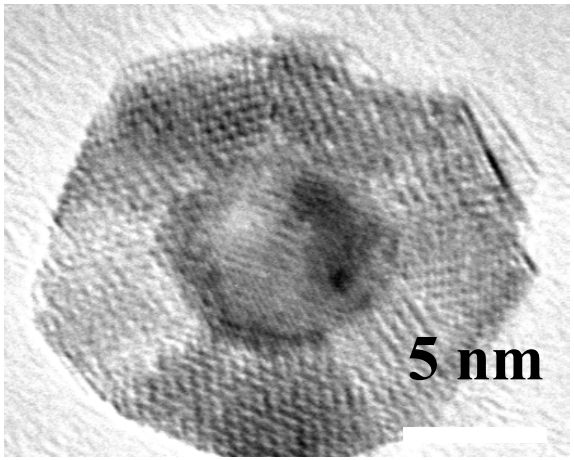
- The oxidation state of ceria nanoparticles change with the environment oxidizing potential of the environment and time.
- The oxidation states alters the in the absorption edge.
- While much of the existing literature is ambiguous in confirming the quantum confinement effects, we find that the variation in the band edge of ceria nanoparticles can be driven by the chemistry (switching of the oxidation state) for particles of consistent size.
- Consistent with the “regeneration” hypothesis used to explain the long effect for oxygen scavenging in biological systems.

We have been studying two types of nanoparticles for environmental cleanup and for medical application

Commercial Nanoparticle



Ion-sputter-gas-aggregate nanoparticles

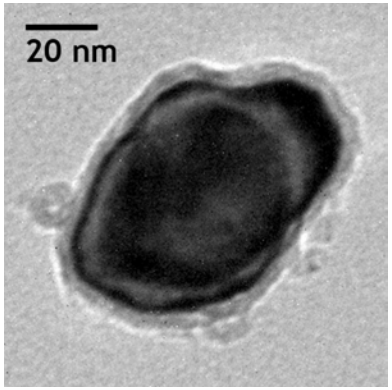


Expose collections of particles to DI water for different amounts of time

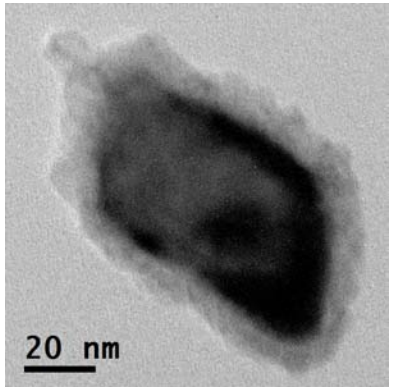
Examine with TEM, XRD, XPS

TEM Images of Nanoparticles after different times of solution exposure

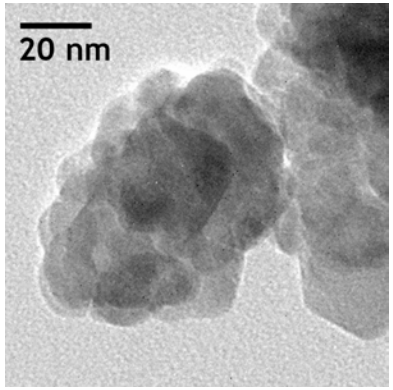
0 day



1 day



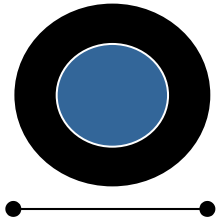
5 day



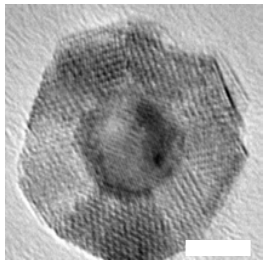
Initially continuous dense oxide shell becomes less dense and other oxide nano-structures form

Shell changes and more oxide forms

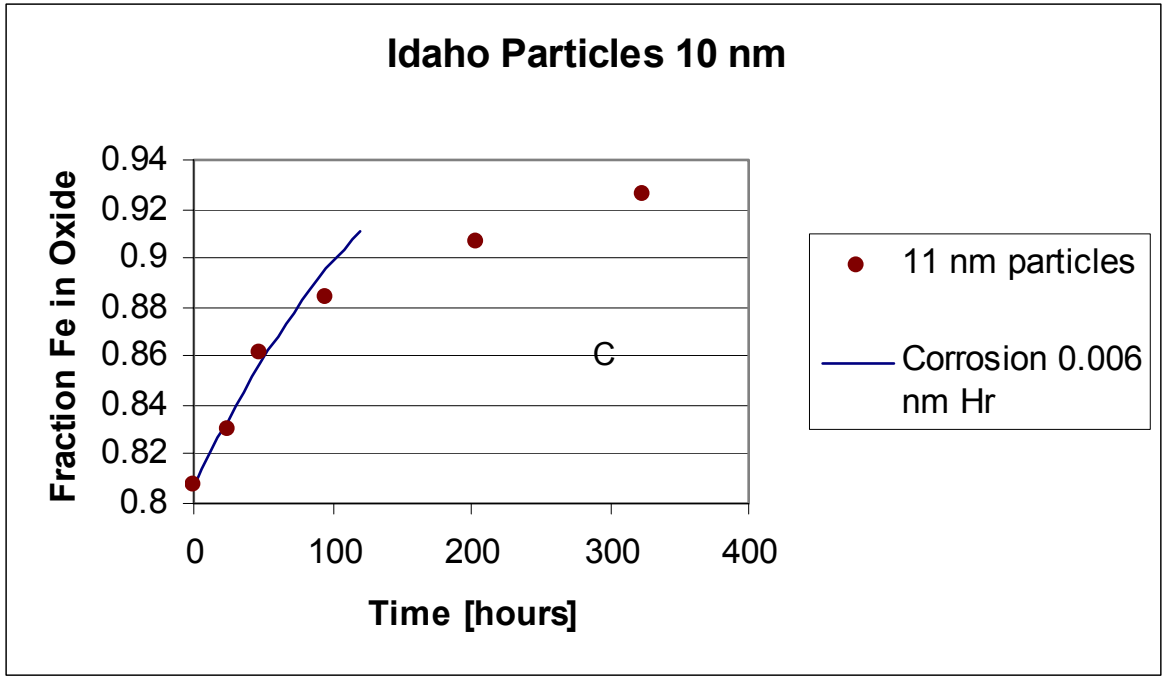
Data and simple model of corrosion



11 nm

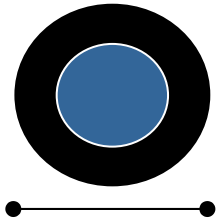


5 nm

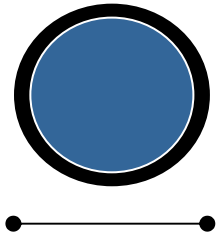


Particles react at rates differ ~ x4

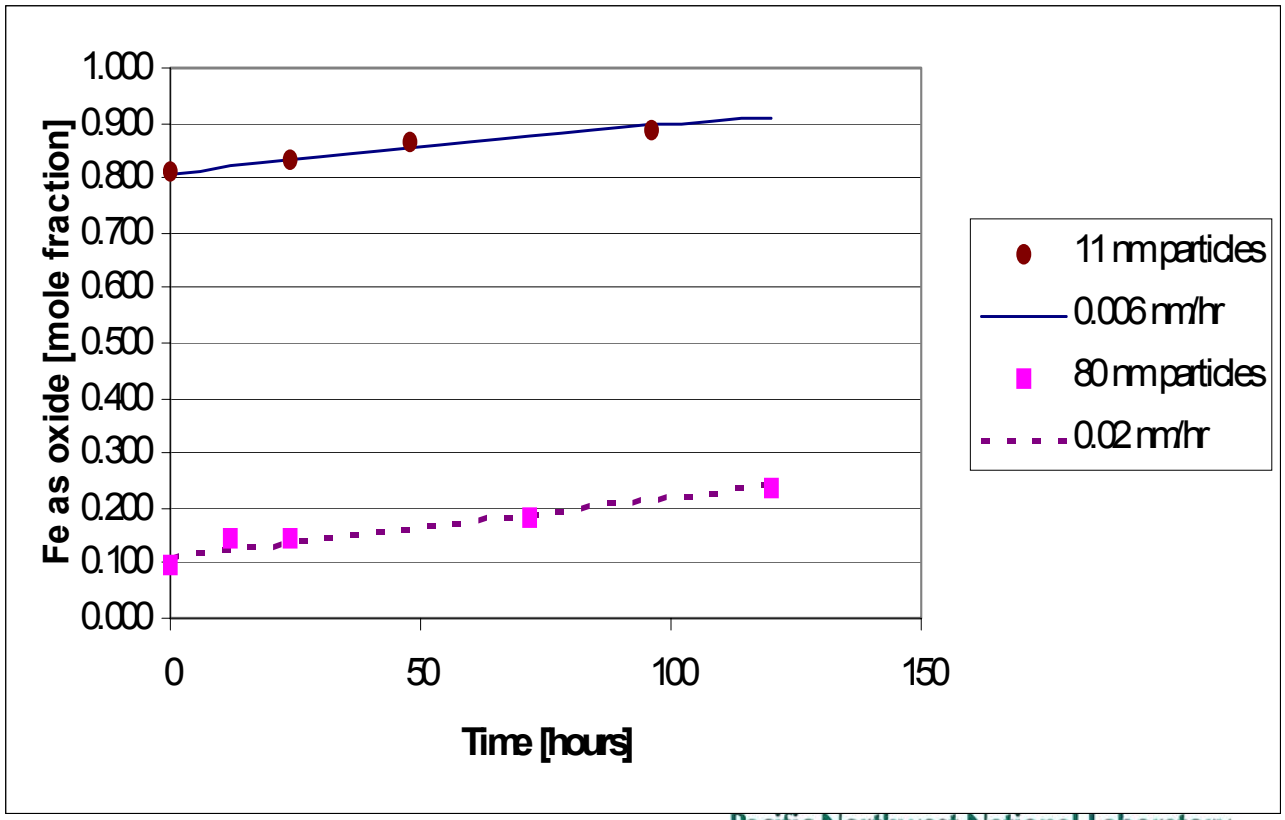
- Slower corrosion rate for the sputter aggregated is stable enough to function as a high magnetic moment particle for thermal cancer treatment
- Does not react with contaminants on time scale of hours.



11 nm



80 nm



Summary and Conclusions

- Many nano-structured materials are dynamic responding to the environment and changing in time. This needs to be considered in the design and application of nanomaterials
- The chemical state of ceria nanoparticles changes in response to environmental conditions over the time of hours and days
- The different reaction rates for different types of iron nanoparticles determine can be designed for the application.
- Characterization, application and consideration of environmental and health effects need to include consideration of stability, environment, processing and time.

Documentary Standards Needs

- Open source terminology in searchable database – fundamental to future of technology – should be freely available
- Guidance documents rather than standards – should all include EHS issue consideration
  - Sample preparation for characterization, including dispersion and aggregation/agglomeration
  - Sample preparation for tox testing
  - Stability considerations relevant to manufactured nanomaterials
  - Application and limitation of surface analysis
  - Expression of concentration and dosimetry
- Database for documentary standards for nanotechnologies – TC 229?

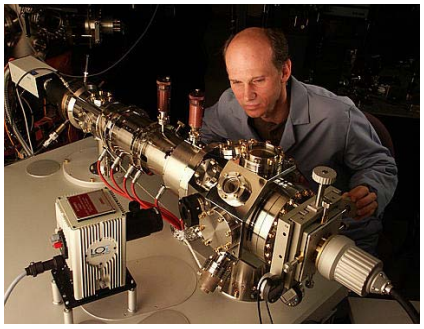
ISO IEC NIST OECD

Nanotechnologies
International Workshop
26-28 February 2008

WR Wiley Environmental Molecular Sciences Laboratory

A national scientific user facility integrating experimental and computational resources for discovery and technological innovation



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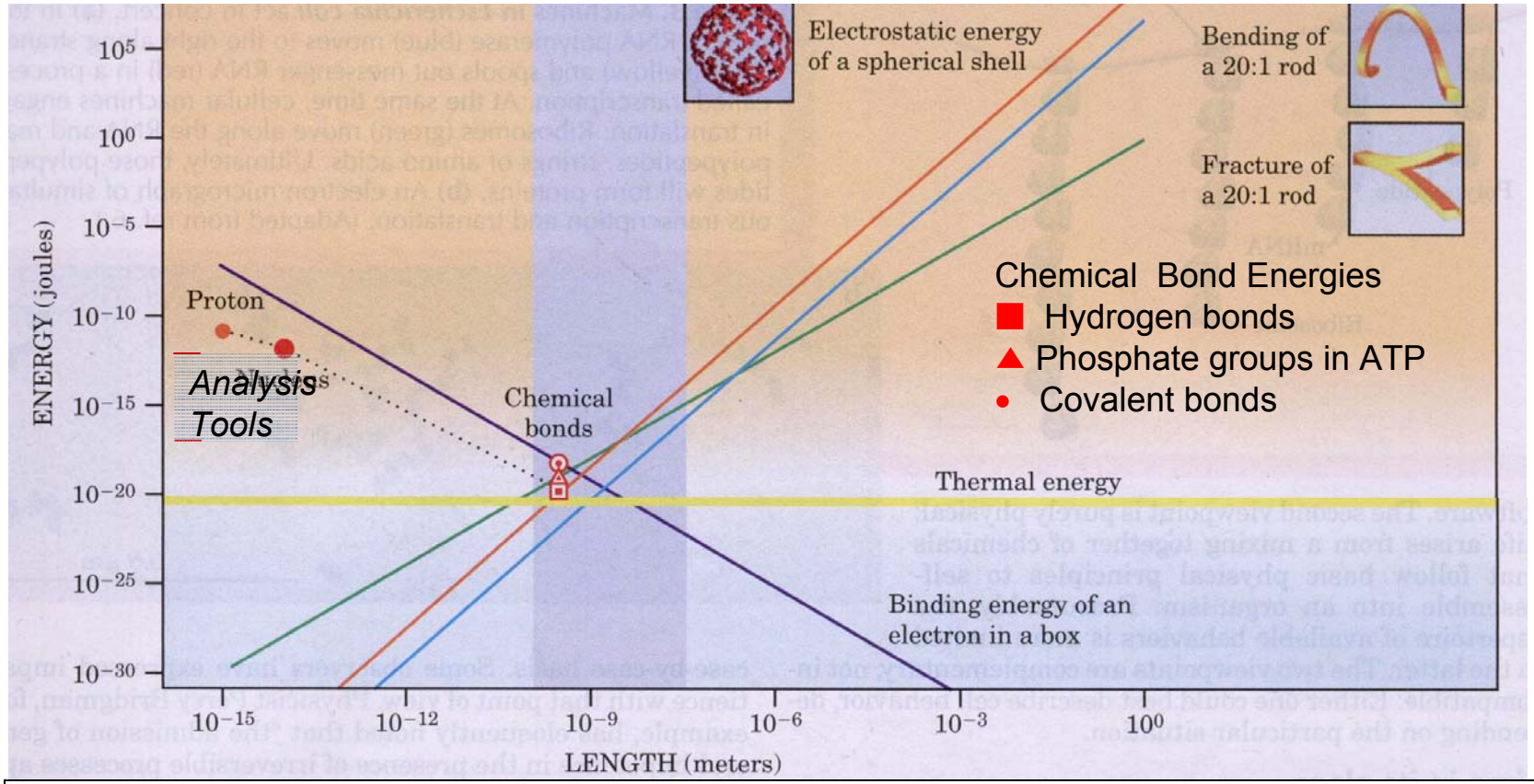
Stability: environmental effects and probe effects

Confluence of Energy Scales

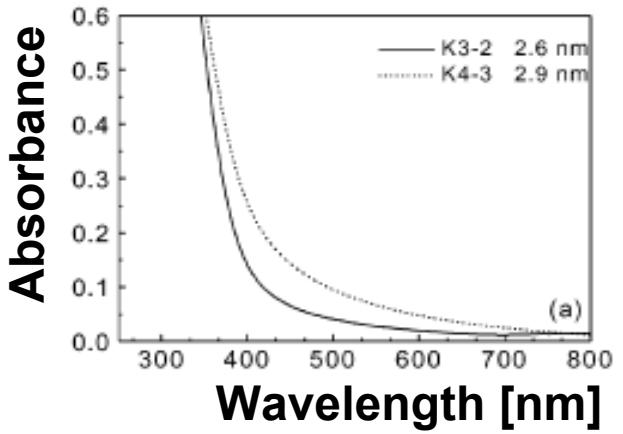
B. Phillips and S. R. Quake, "The Biological Frontier of Physics" Physics Today May 2006

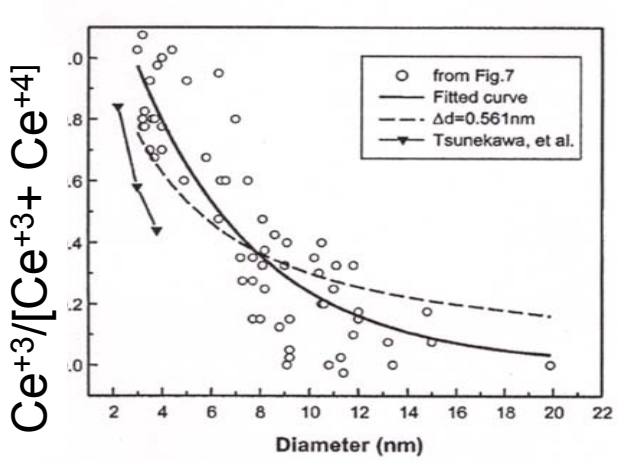


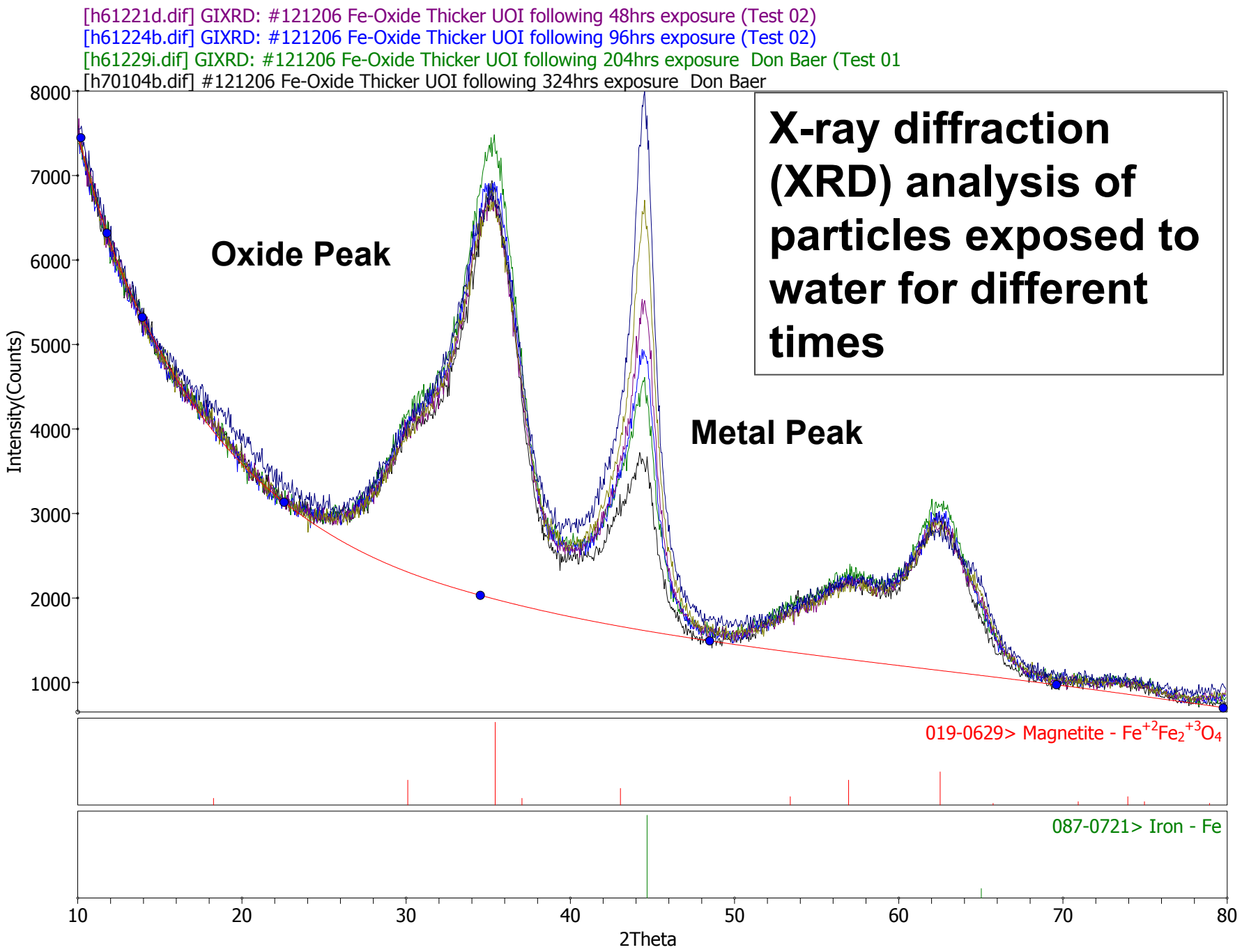
Variations of thermal, chemical, mechanical and electrostatic energies as a function of the size of an object. "*As the characteristic size approaches that of biological macromolecules [also nano-size objects], all energy scales converge. This convergence is an opportunity for complex physical phenomena and processes that are utilized by life*."

Contradictory reports in the literature

- Data reported measuring quantum confinement inconsistent
  - Seen in different size ranges (or not seen) by different groups
- Ceria known to be an oxygen storage material
  - Change from Ce^{+4} to Ce^{+3} with size
  - Ease of change in oxidation state in different conditions
- Can some of the inconsistencies be due to processing and environmental effects?






[h61221d.dif] GIXRD: #121206 Fe-Oxide Thicker UOI following 48hrs exposure (Test 02)
[h61224b.dif] GIXRD: #121206 Fe-Oxide Thicker UOI following 96hrs exposure (Test 02)
[h61229i.dif] GIXRD: #121206 Fe-Oxide Thicker UOI following 204hrs exposure Don Baer (Test 01
[h70104b.dif] #121206 Fe-Oxide Thicker UOI following 324hrs exposure Don Baer
X-ray diffraction (XRD) analysis of particles exposed to water for different times
Oxide Peak
Metal Peak
Intensity(Counts)
8000
7000
6000
5000
4000
3000
2000
1000
019-0629> Magnetite - Fe+2Fe2+3O4
087-0721> Iron - Fe
10
20
30
40
50
60
70
80
2Theta

Ce 3d photoelectron peaks from a solution aged one day (solid curve) and a solution aged several weeks (dashed curve) consistent with Optical Absorption data