Scientific Innovation Through Integration

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National Nanotechnology Initiative Workshop

Nanomaterials and Human Health & Instrumentation, Metrology, and Analytical Methods Workshop

November 17&18, 2009, Arlington, Virginia

Nanomaterials Characterization Obstacles

Examples highlighting a subset of issues already identified

Don Baer+ many collaborators

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Iron Metal-Core /Oxide-Shell and Ceria Nanparticle Examples

1) Nano-particulate iron has several current and potential applications:

- Ø Medical - imaging, diagnosis, and treatment,
- Ø Magnetic storage
- Ø Environmental remediation

Our application is for environmental remediation
Highlights several analysis challenges (surface chemistry, contamination, environmental conditions, and dynamic properties)

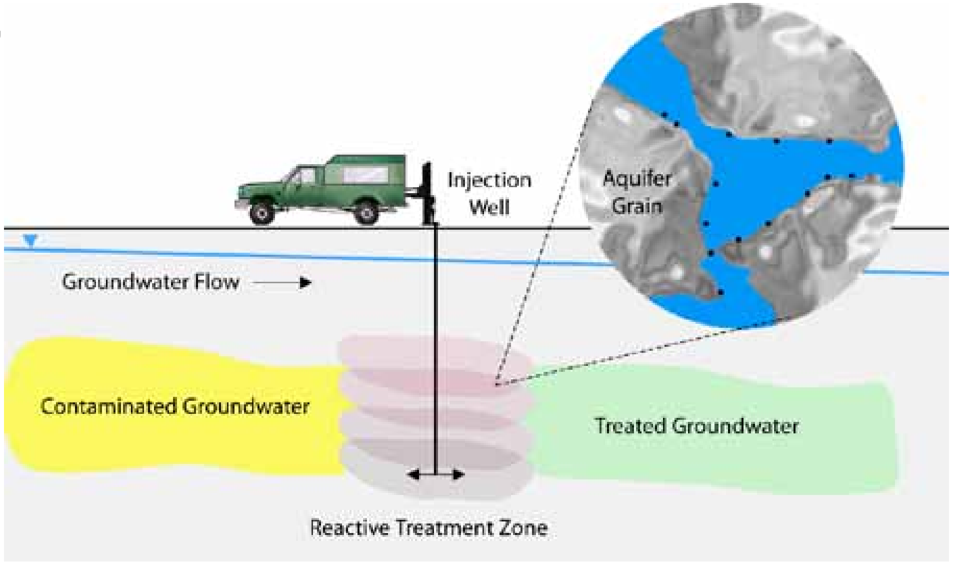
2) Nanoparticles of Ceria (cerium oxide) have application in several areas including catalysis, fuel cells, radiation protection and cancer treatment:

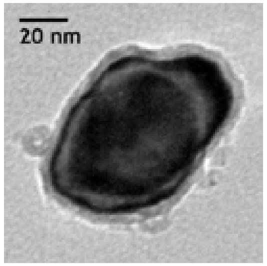
Highlight environmental and solution effects

Reaction properties of iron nanoparticles in solution

Nano zero valent iron (nZVI) for contaminant removal

- Reacts to reduce contaminants, such at CCl_4
- Can be inserted into the subsurface
- Important issues include:
  - Controlling the reaction products
  - How structure and properties change with time (i.e., aging)
  - Tuning the particle properties

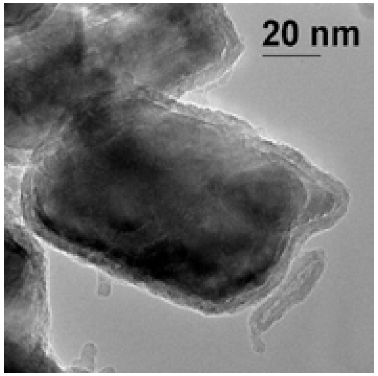




Tratnyek and Johnson (2006) *NanoToday* 1:44

Analysis Issues

- Need to determine **reaction pathway** in context of **particle characteristics (structure/function)**
- Reactive metal-core and oxide-shell particles change with **time** and react with the **environment**
- Need to monitor in **real-time** properties **in solution**
- Require **detailed information** about particles, beyond what is often available for in situ methods
- Need to assure that **ex situ methods** are obtaining **accurate information –** challenge of particle extraction from solution



Nanoparticles are not created equal

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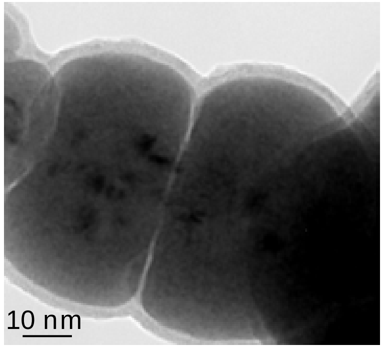
Fe metal-core oxide shell particles produced by different processes have different surface chemistry and shell structures that give rise to different CCl_4 interaction products

Toxic **a**
breakdown products

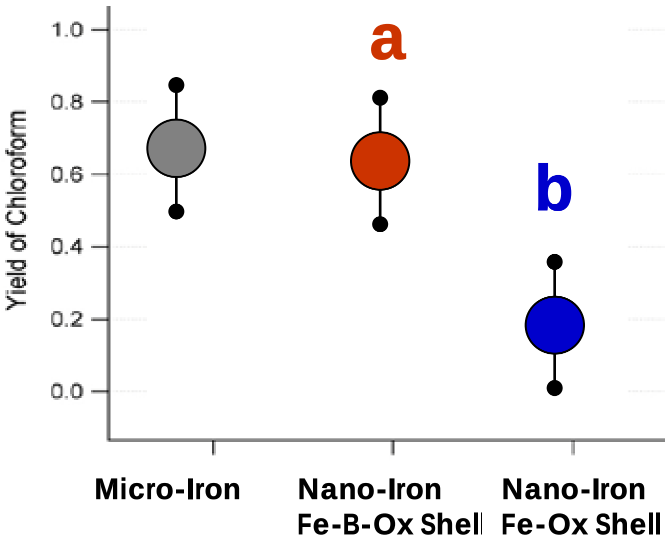


CCl_4 (CT) $\xrightarrow[-1\ Cl^-]{+1\ e^-}$ $\bullet CCl_3$

$\bullet CCl_3$ $\xrightarrow{+\bullet H}$ $HCCl_3$ (CF)

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

Benign **b**
breakdown products



Nurmi et al. (2005) *ES&T* 39:1221-1230

Reactivity not highly dependent on size

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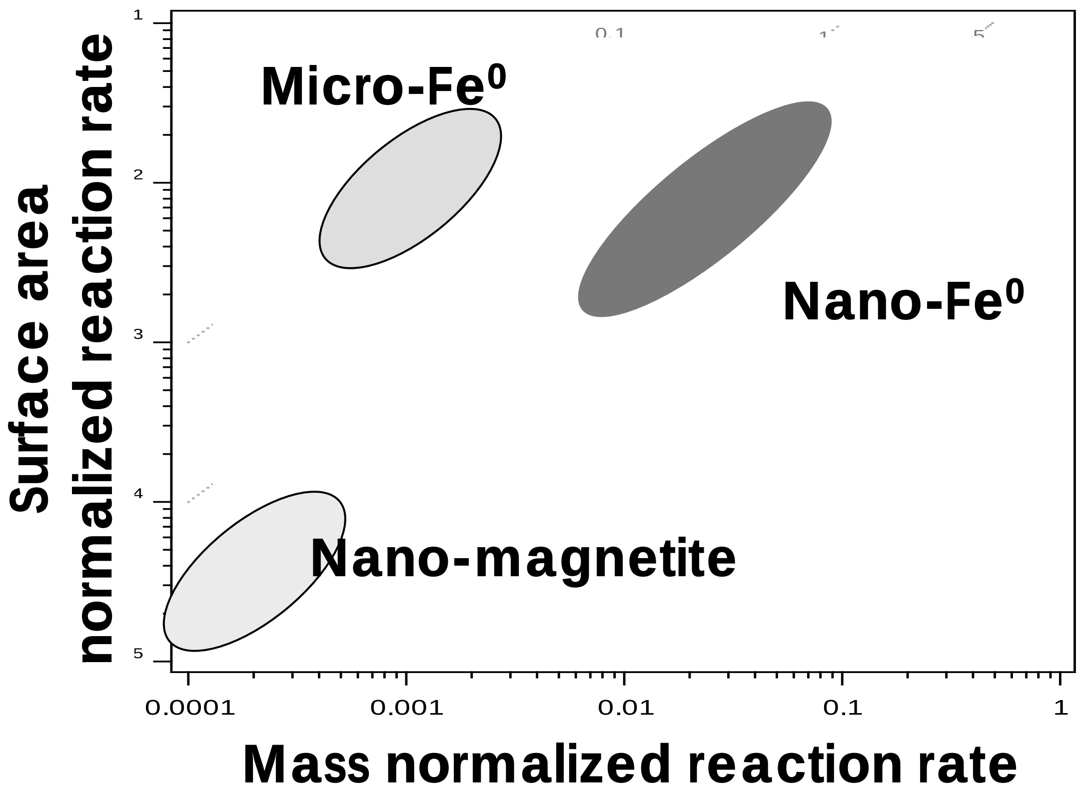
- Surface area normalized reaction rate independent of size for micro and nano metal core oxide shell particles
- Reactivity of particles without metal significantly slower

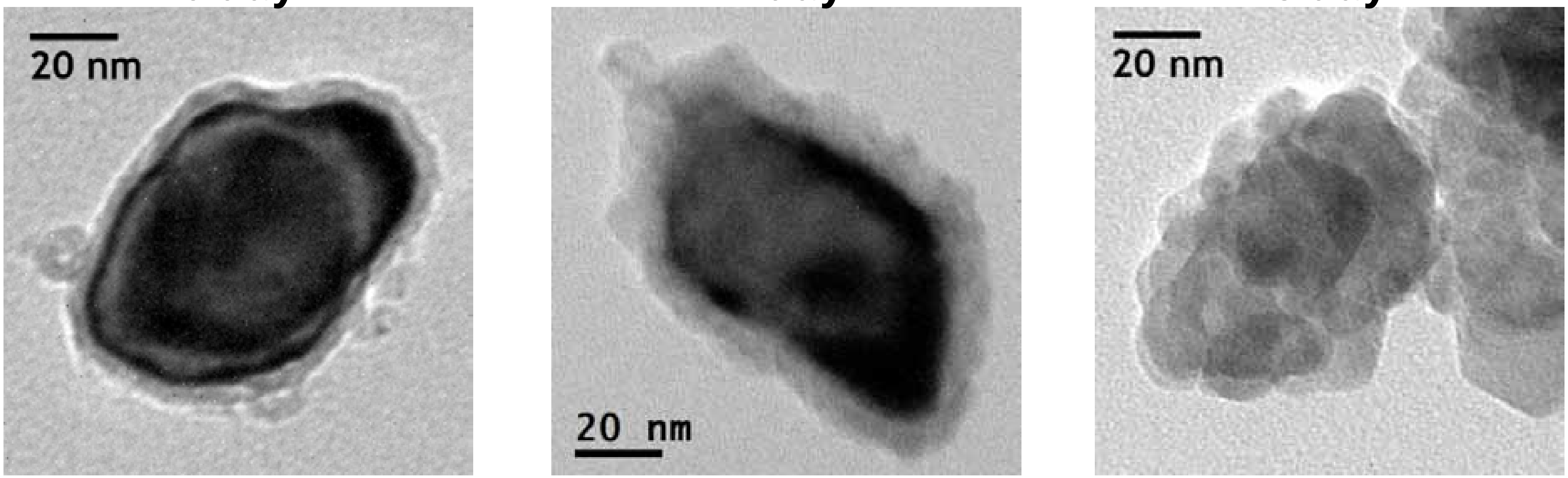


Nurmi et al. (2005) *ES&T* 39:1221-1230

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

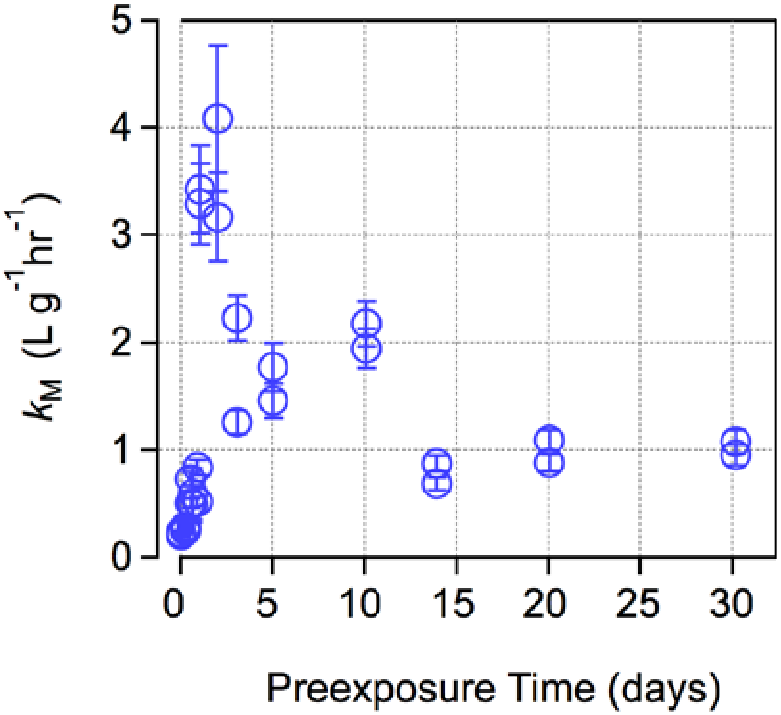
Sarathy et al. (2008) *J. Phys. Chem. C* 112, 2286-2293

Reactivity varies as particles change

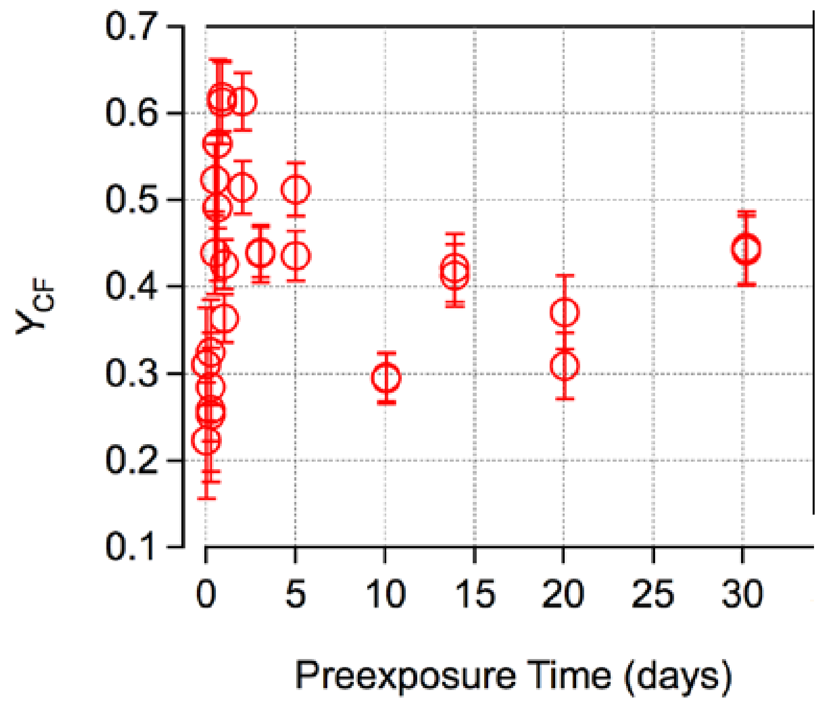
Batch interaction with CCl_4

Both the reaction rate and products formed change with time in solution

Reaction rate



CF yield



Sarathy et al. (2008) *J. Phys. Chem. C* 112 2286-2293

Influence of natural organic material (NOM) on particle oxidation/corrosion

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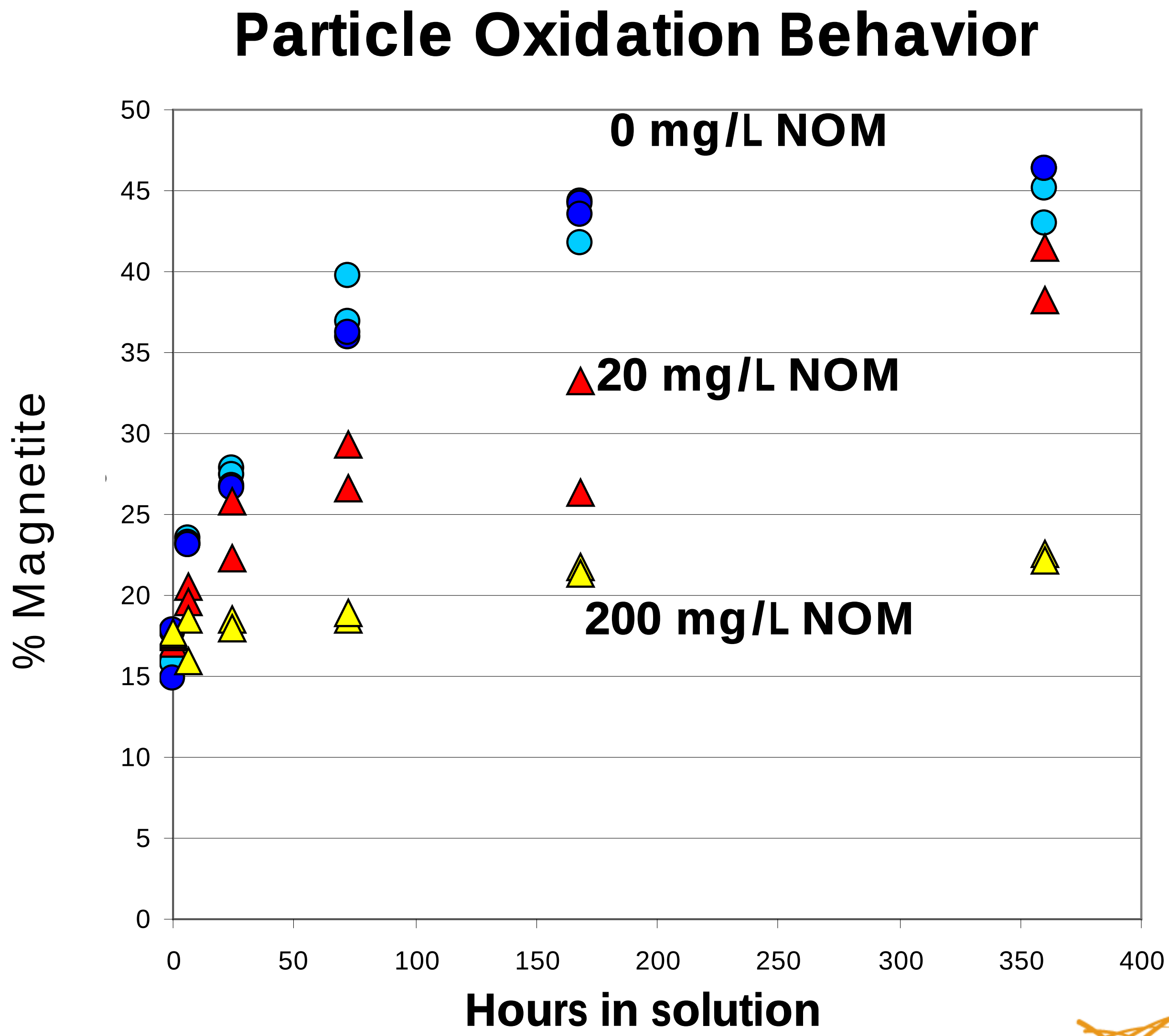
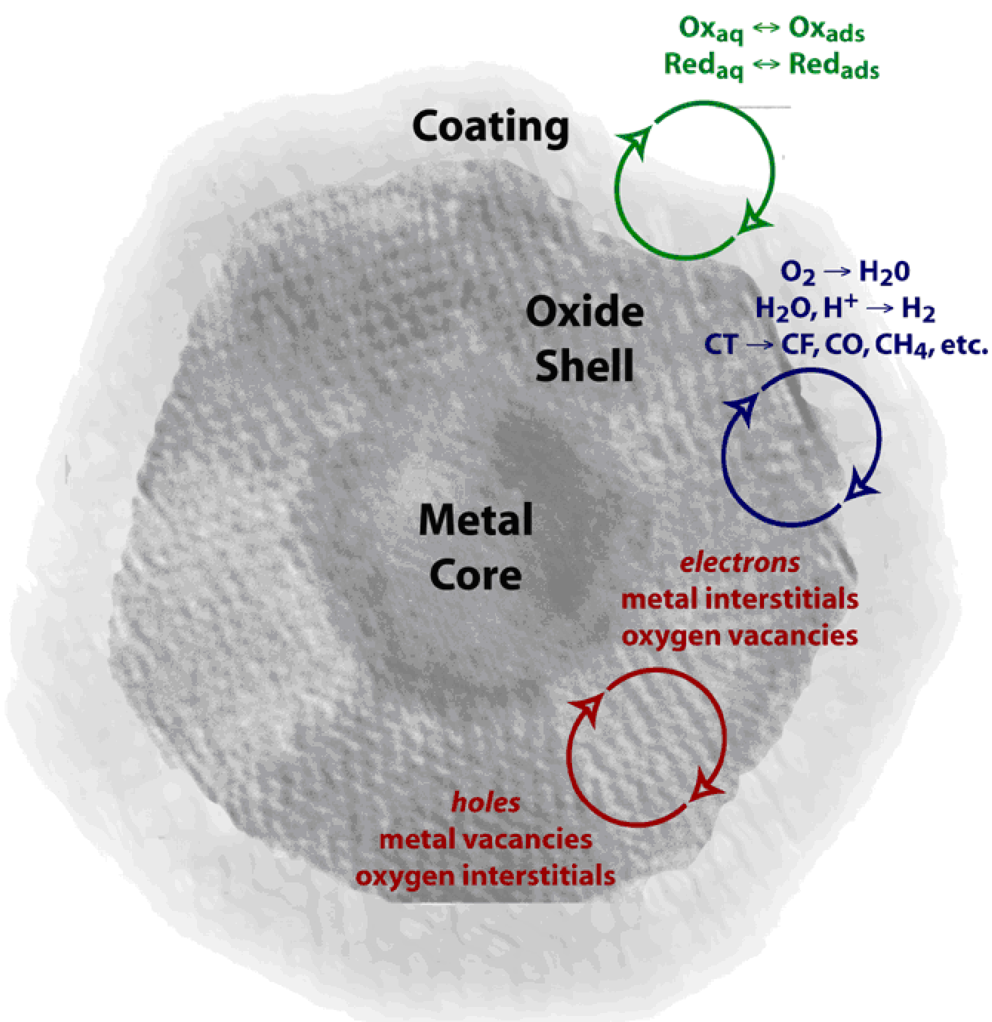


Behavior of nanoparticles depends on particle structure and history

- 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



Summary – Iron Particles (apply widely)

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- Similar nanoparticles can have significantly **different behaviors** due to **synthesis process** as well as **dopants** and **contaminants**
- **Surface chemistry** and functional groups play a major role in particle behavior
- Many properties of nanoparticles are **dynamic** in that they change with **time** and **environment**.
- **In situ** measurements are important for understanding particle behavior (we use XRD, electrochemistry and reaction measurements).
- Sample **processing** (drying and other treatments) can alter particles and change analysis results, but **ex situ** tools (especially surface chemistry tools) are **needed** to understand properties
- Nanoparticles can be **unstable as synthesized**. Therefore, aging may not require environmental effects, but only time

Why Cerium oxide (Ceria, CeO_2)

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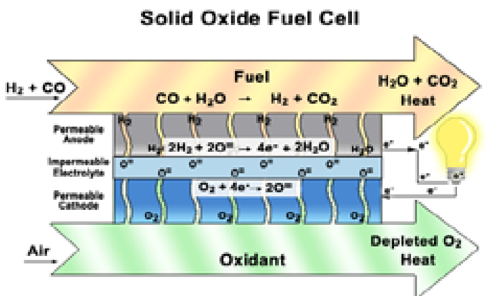
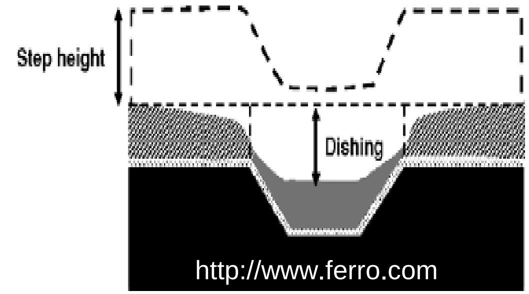
Solid Oxide Fuel Cells	Catalysis	Microelectronics (CMP)
(Ce 3+ and Ce 4+)	*(Ce3+ and Ce4+)*	*(Ce3+)*



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



Films or powder pellets — Particles — Particles

Bio-medical Applications

(Ce3+ and Ce4+)

Particles

UV-protection Cancer treatment

Many Examples of Health Related Research

Model Study	Publication
Radiation Protection	Nano Letters 2006
Retinal Degeneration	Nature Nanotech 2006
CNPs and Y2O3 are Neuroprotective	BBRC 2006
Superoxide Dismutase	Chem Comm 2007
Protection to neuron Cells	Biomaterials 2007
pH dependent Antioxidant Property	Small 2008
Ceria-Zirconia as antioxidant materials	Nanomedicine 2008
CNPs as Catalase Mimetic	Chem Comm 2009 (submitted)
Protection against radiation induced Pneumonitis	Nanomedicine 2009
Oxidase like activity of CNPs (dextran coated)	Angew. Chemie 2009
Anti-inflammatory property of CNPs	Small 2009
Neuron Survival in Alzheimer's Model	Current Nanoscience 2009
PEG CNPs as SOD and Catalase Mimetic	JACS Comm 2009

However!! **Toxicity Reports**

Model Study	Publication
Toxicity of Cerium oxide nanoparticles in lung cells	International Journal of Toxicology 2006
Oxidative stress induced by cerium oxide nanoparticles in Beas -2B cells	Toxicology 2008
Oxidative stress of Ceria nanoparticles in bronchial epothelial cells	Toxicology Letters 2009

Characterization and Preparation Issues:

- Ø A variety of different effects (positive and negative) observed for different preparation methods
- Ø Nature of particles in Ce^{+3} and Ce^{+4} oxidation unclear and leading to apparently some wrong conclusions

Cerium Oxide Nanoparticles

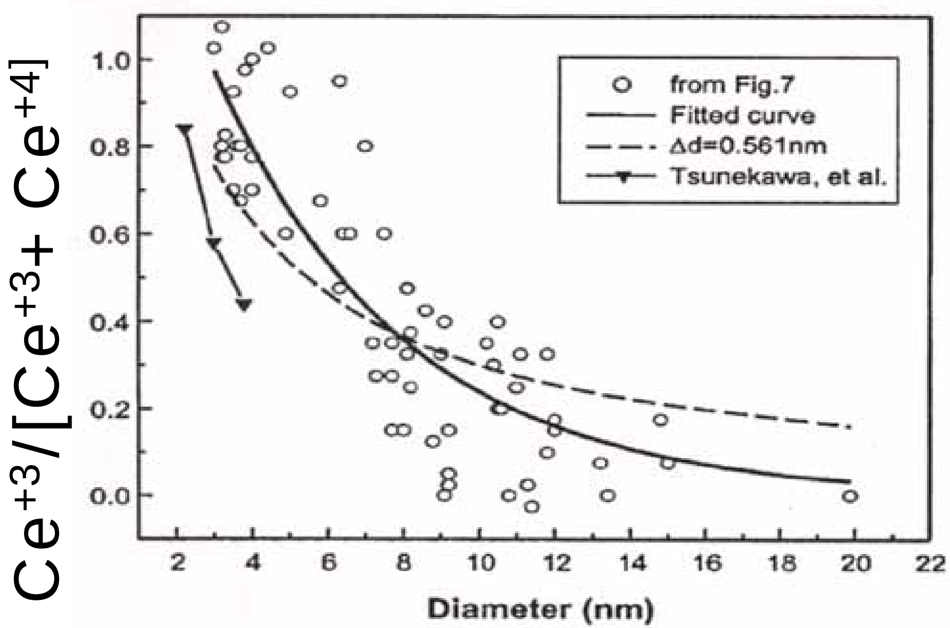
- **Studies indicate that as particles approach the nanosize Ce^{+3} is formed in addition to**

PHYSICAL REVIEW B 69, 125415 (2004)

Oxidation state and lattice expansion of CeO_{2-x} nanoparticles as a function of particle size

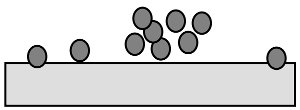
Lijun Wu, H. J. Wiesmann, A. R. Moodenbaugh, R. F. Klie, Yimei Zhu, D. O. Welch, and M. Suenaga
Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA

From EELS TEM data

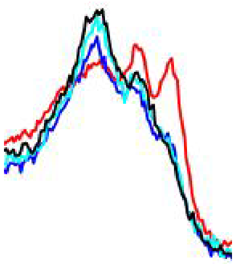


TEM, XPS and Optical Measurements at PNNL and UCF

- Observed chemical state of particles depends on particle size, formation process, and material loading on a substrate



- By changing the oxygen potential in solution it is possible to cycle the chemical state of the particles between Ce^{+3} to Ce^{+4} (environmental effect)
- Color and optical adsorption measurements show switch form Ce^{+3} to Ce^{+4} and back



Mixed Ce^{+4} Ce^{+3} Ce^{+4}

XPS and TEM Analysis

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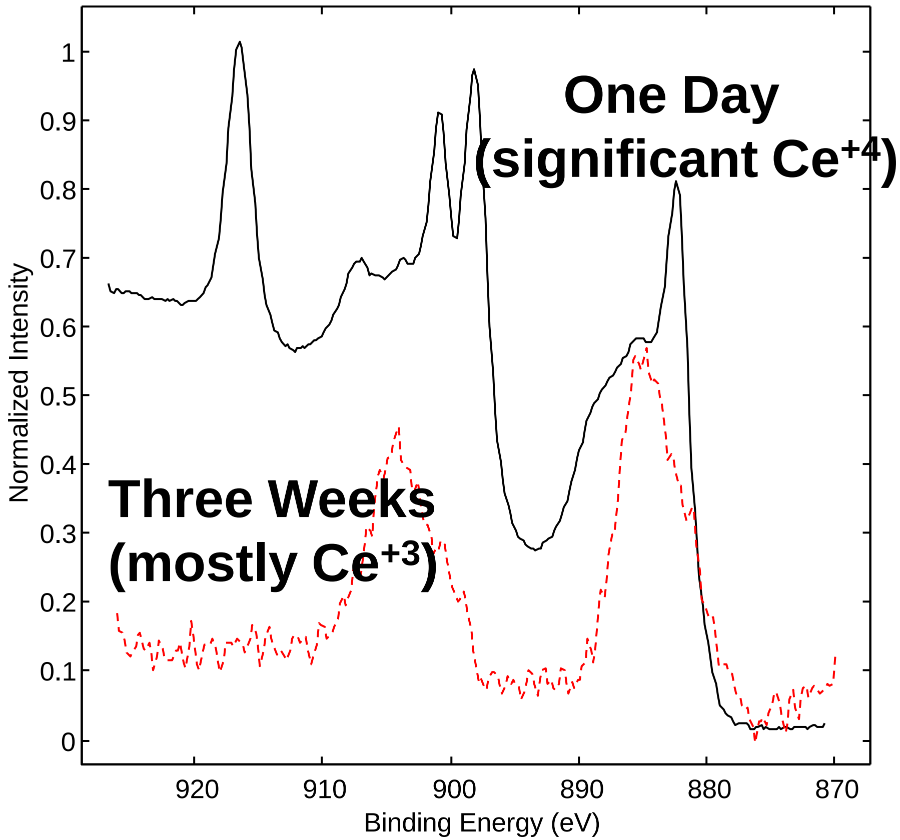
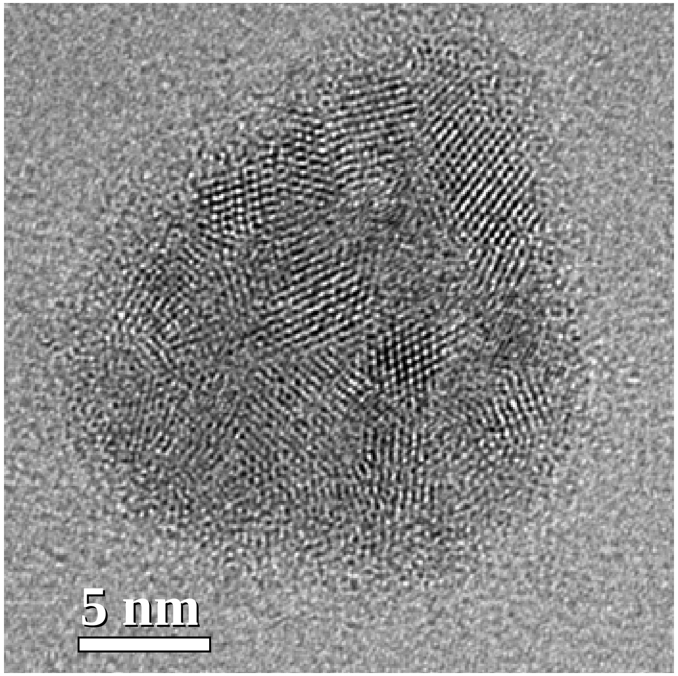
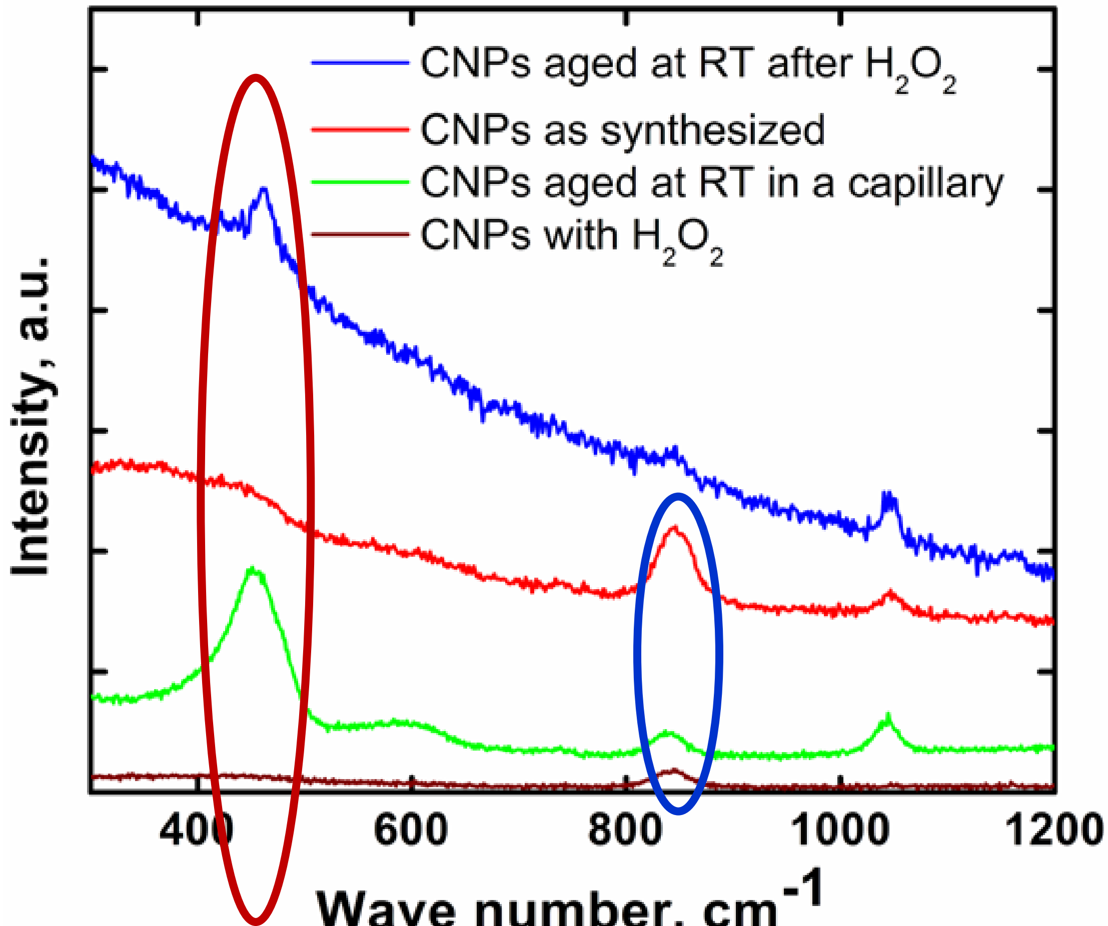
- Oxidation state from ex situ XPS data consistent with optical data



- TEM data shows 10-20 nm agglomerates made up of 3 to 5 nm particles for most conditions



Raman spectra – CNPs + H_2O_2



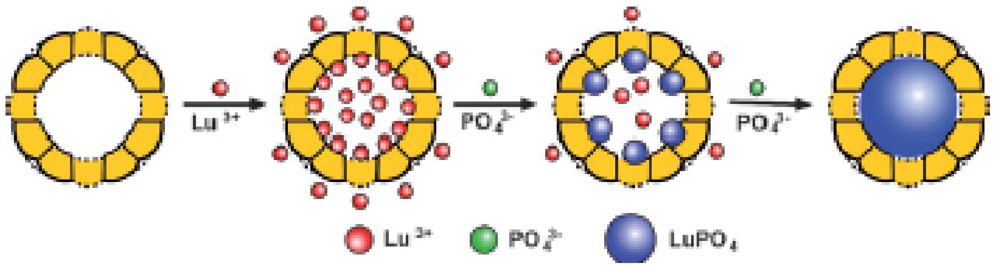
- Formation of a cerium peroxide complex
- Regeneration of CeO_2 peak

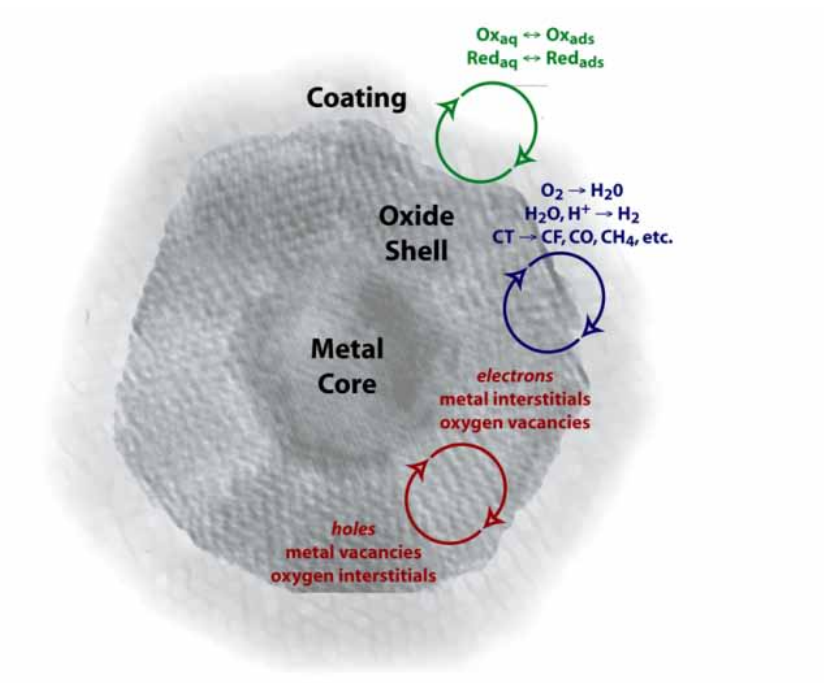
Ceria Particle Observations (still working to fully understand)

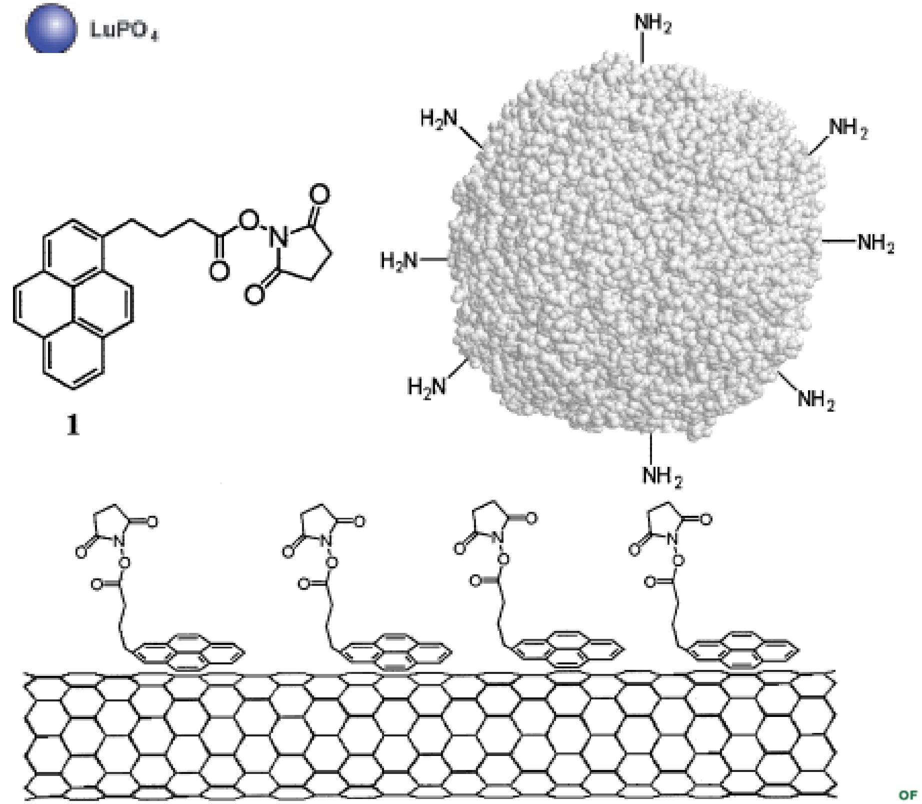
- Peroxide state appears only for small particles (< 40 nm)
- For 3 to 5 nm particles, the CeO_2 Peak disappears when peroxide present and returns on aging
- Measurements appear to contradict the TEM observations, but consistent with XRD done in solution
- *'Particles'* in solution have a much more complex chemistry than initially thought
- Ceria measurements highlight importance of environment, time and *in situ* measurements

Surface and Near Surface Tools Critical to Nanoparticle Characterization

Surfaces layers and attached molecules play important role







XPS, SIMS, AES important

Grainger and Castner Review Article Highlights Importance of Surfaces

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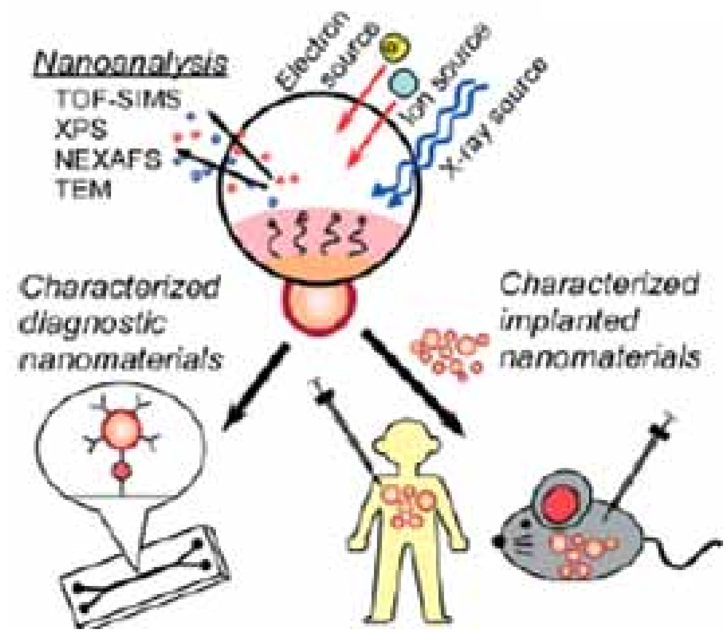
- Nanomaterials advocated for biomedical applications *must exhibit well-controlled surface properties*
- Dispersed materials with extremely high specific surface areas *require as extensive characterization* as their macroscale biomaterials analogues
- *Emphasis on reporting rigorous surface analysis or characterization*
- *Surface contamination* is likely, given their processing conditions and interfacial energies
- In situ analysis and analysis soon after synthesis are important

DOI: 10.1002/adma.200701760

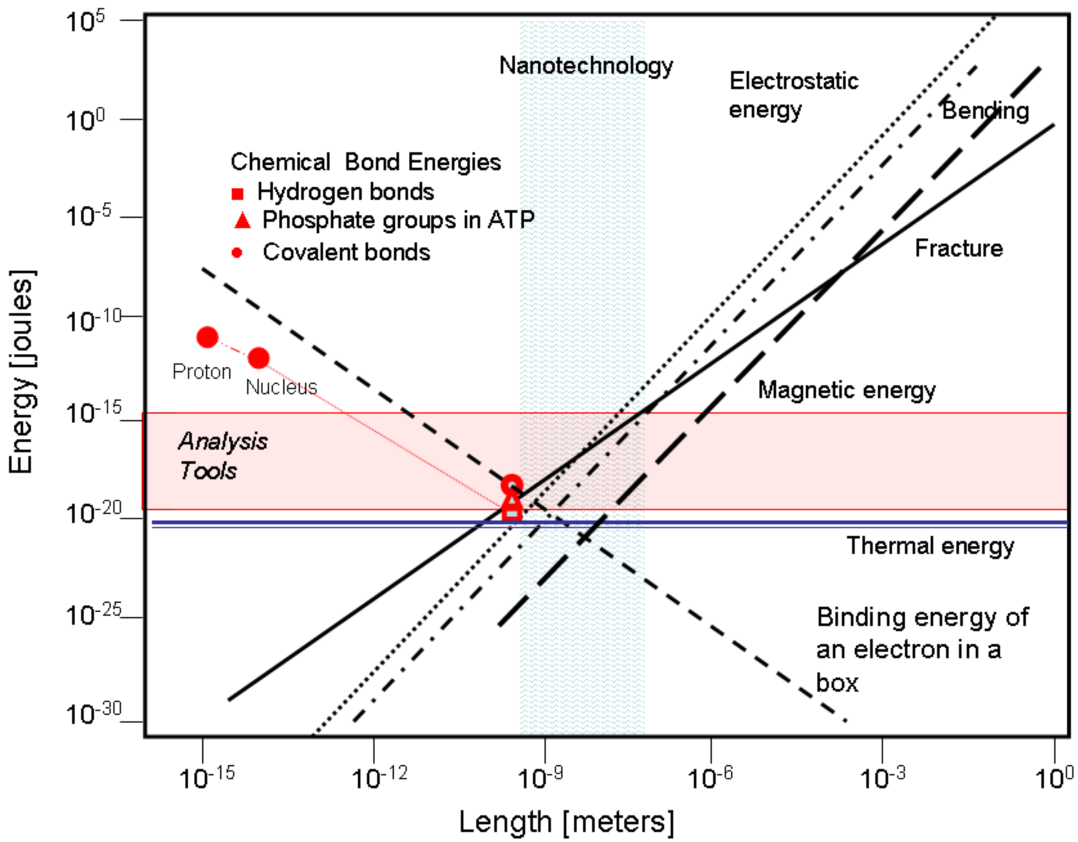
Nanobiomaterials and Nanoanalysis: Opportunities for Improving the Science to Benefit Biomedical Technologies**

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



Grainger and Castner, Advanced Materials 20 (5) (2008) 867–877

Different types of particle energy converge at the nanometer size



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

- 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

Summary and opinions - Characterization

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- 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) (see AS+NS-WeM9).
- *Great need for **real-time** measurem*ents 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

Characterization and Metrology
(adapted from C. R. 'Dick' Brundle from electronic industry)

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- **Characterization** (Electronics Industry/Nanomaterials)
  - "Determining enough about the "product" so that it can be successfully made (right properties), and is durable. "
  - For nanomaterials this may mean learning enough about a particular nanomaterial system to understand what attributes and characteristics impact desired performance and what characteristics can impact human health.
  - Often a slow careful process requiring a high level of expertise
- **Metrology**
  - In principle, once "enough: has been established from the characterization, metrology is putting into place measurements which "quantify" those attributes considered important." Should mean those which affect functional properties.
  - Once the important characteristics of a specific nanomaterial are identified (through characterization and functional tests) a subset of measurements can be used to determine the status of a particular nanomaterial.
  - Should involve rapid and well defined measurement processes not requiring expertise

Acknowledgements

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EMSL - William R. Wiley's Vision: An innovative multipurpose user facility providing "***synergism between the physical, mathematical, and life sciences.***"

Dr. William R. Wiley
PNNL Director

- A large portion of the research was performed using EMSL, a national scientific user facility sponsored by DOE-BER and located at Pacific Northwest National Laboratory. New capabilities that might allow you to expand scope of your research (with no instrument charge)- see booth in vendor show.
- Research was supported by the U. S. Department of Energy Offices of Biological and Environmental Research (BER) and Basic Energy Science (BES)
- *Many* different colleagues participated in different portions of the work

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William R. Wiley EMSL Environmental Molecular Sciences Laboratory

ECASIA 2007

Brussels Belgium, September 2007

Characterization Challenges for Nanomaterials

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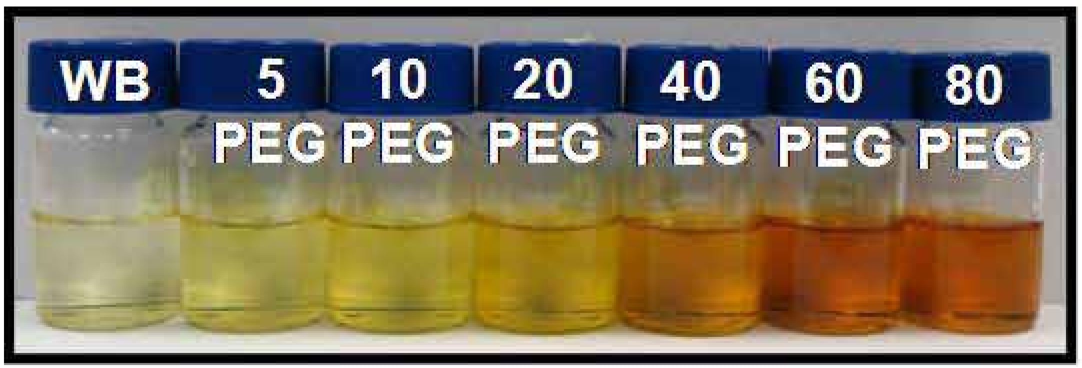
Nanocerium Oxide as Antioxidant – Role of Environment and Surface Coating on the Interaction with Reactive Oxygen Species

Ajay S. Karakoti, Sanjay Singh, Amit Kumar, Satyanarayana V.N.T. Kuchibhatla, William T. Self and Sudipta Seal
University of Central Florida
Pacific Northwest National Laboratory



Presented by
Ajay S. Karakoti

Surface Engineering and Nanotechnology (SNF) Lab
Advanced Materials Processing and Ananlysis center (AMPAC)

"Bridging the technology gap"

Scientific Innovation Through Integration

Ceria Nanoparticles (CNPs)

Influence of Aging and Local Environment

Satyanarayana V.N.T. Kuchibhatla, A.S. Karakoti, Ch. F. Windisch Jr, P. Nachimuthu, T. Varga, S. Seal, S. Thevuthasan, D. R. Baer

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"Every attempt to understand ceria leads to many more questions"

- Don Baer