Imaging and Structure of Quantum Dots, Nanoparticles and Aerogels

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Outline

Quantum Dot Synthesis Methods

Quantum Dot Optical Properties

Nanoparticle Synthesis (Ablation)

Aerogel Synthesis and Lipid Bilayers

Quantum Dot Materials Science

- The synthesis of quantum dots in semiconducting systems: an exciting theme in materials research at the bio-nano-computational interfaces
- Many aspects: Synthesis, nanostructure characterization, MD computer simulations, and bio-applications
- Materials are either clusters of QD (nanocrystals) or structures embedded in glasses, polymers and gels
- Scientific issues:
  - Control and tailor the size of nanoscale building units
  - Characterization of nanoscale structure and chemistry

Quantum Dots in Glass

- Traditional methods of semiconductor nanocrystals growth rely on long furnace treatments
- For example:
- Glass Melting & casting: 1300-1400 C
- Reheat Temperature : 500-1000 C

Synthesis of Quantum Dots (Nanocrystals) in Glasses

Finely ground glass powder + semiconductor powder

Co-melting above liquidus temperature

Dissolution of mixture to form melt

Casting into shapes/fibers

Striking (heat treatment)

Structural/optical/mechanical characterization

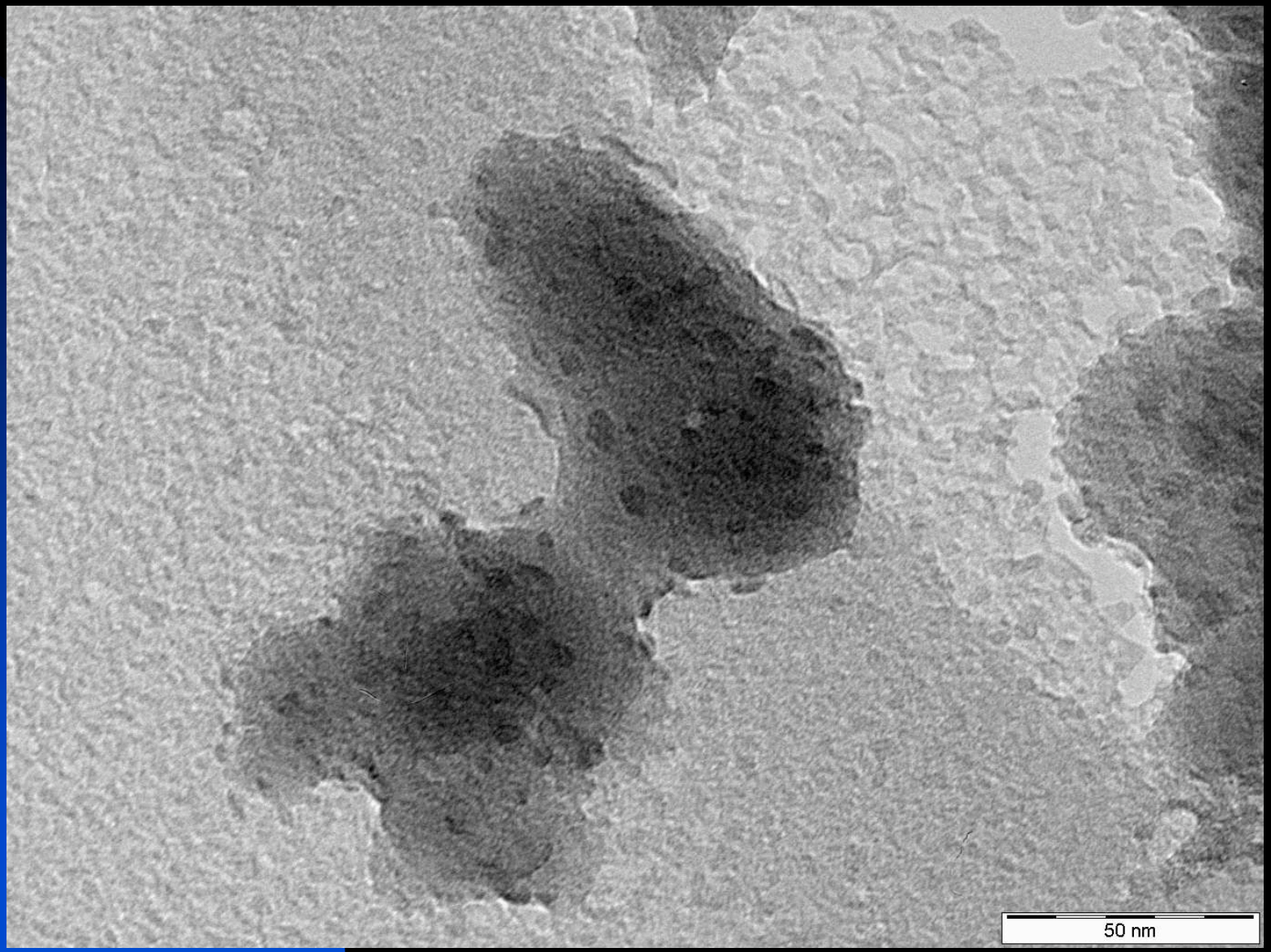
QD Synthesis Methods

- Melt and Cast Glass and reheat
- Chemical Precursors, Sol-gel
- Ablation and Flame Synthesis
- QD in Polymer Cavities
- Laser Heated Microspheres

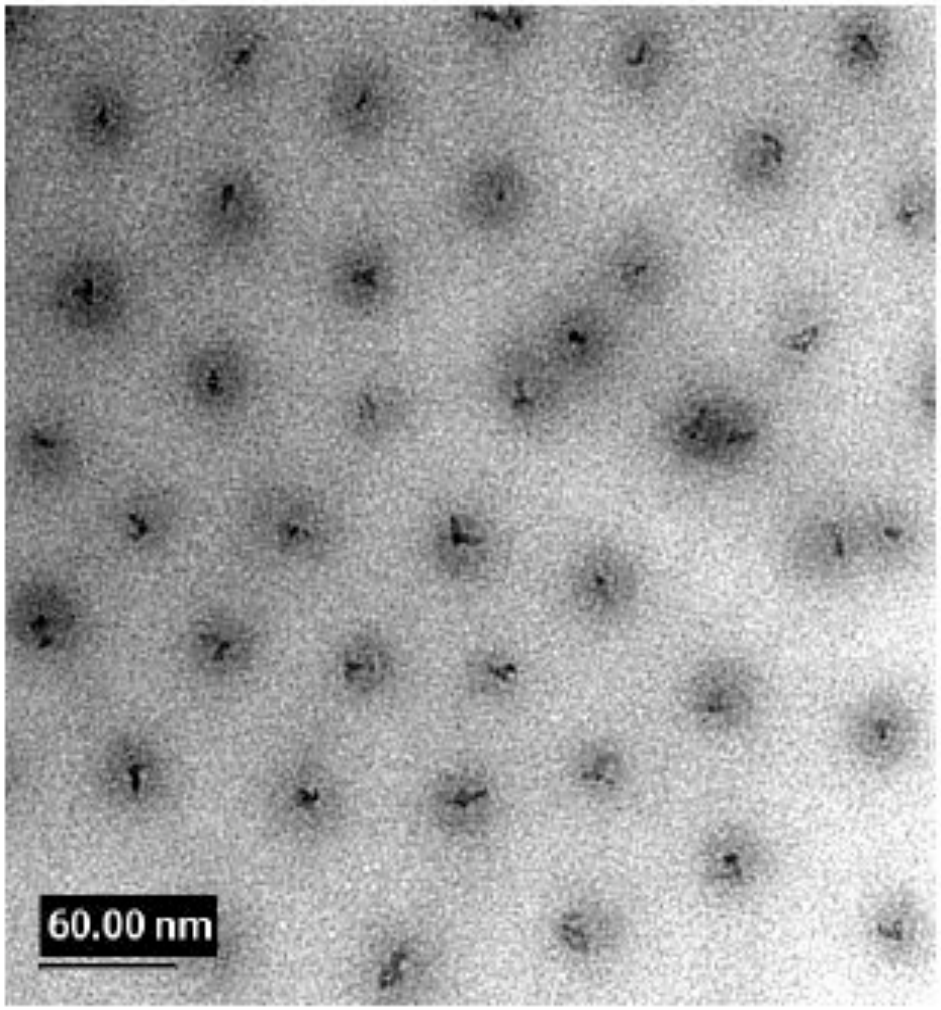
Characterization

- Imaging of Quantum Dots Processed in Glasses and Polymers (TEM, SEM, AFM)
- Rare earth Nanoparticles made by flame synthesis (EELS/XAS)
- Aerogels for biomembranes (AFM)

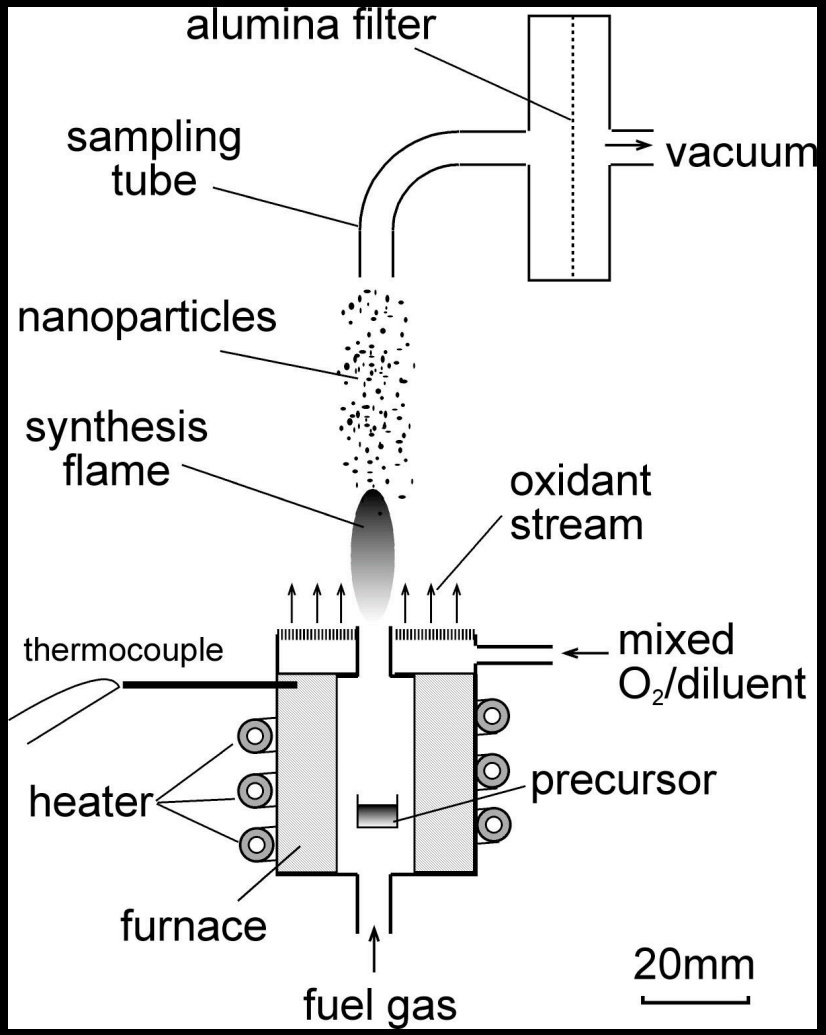
TEM of CdTe QD in Glass (Laser Heating)



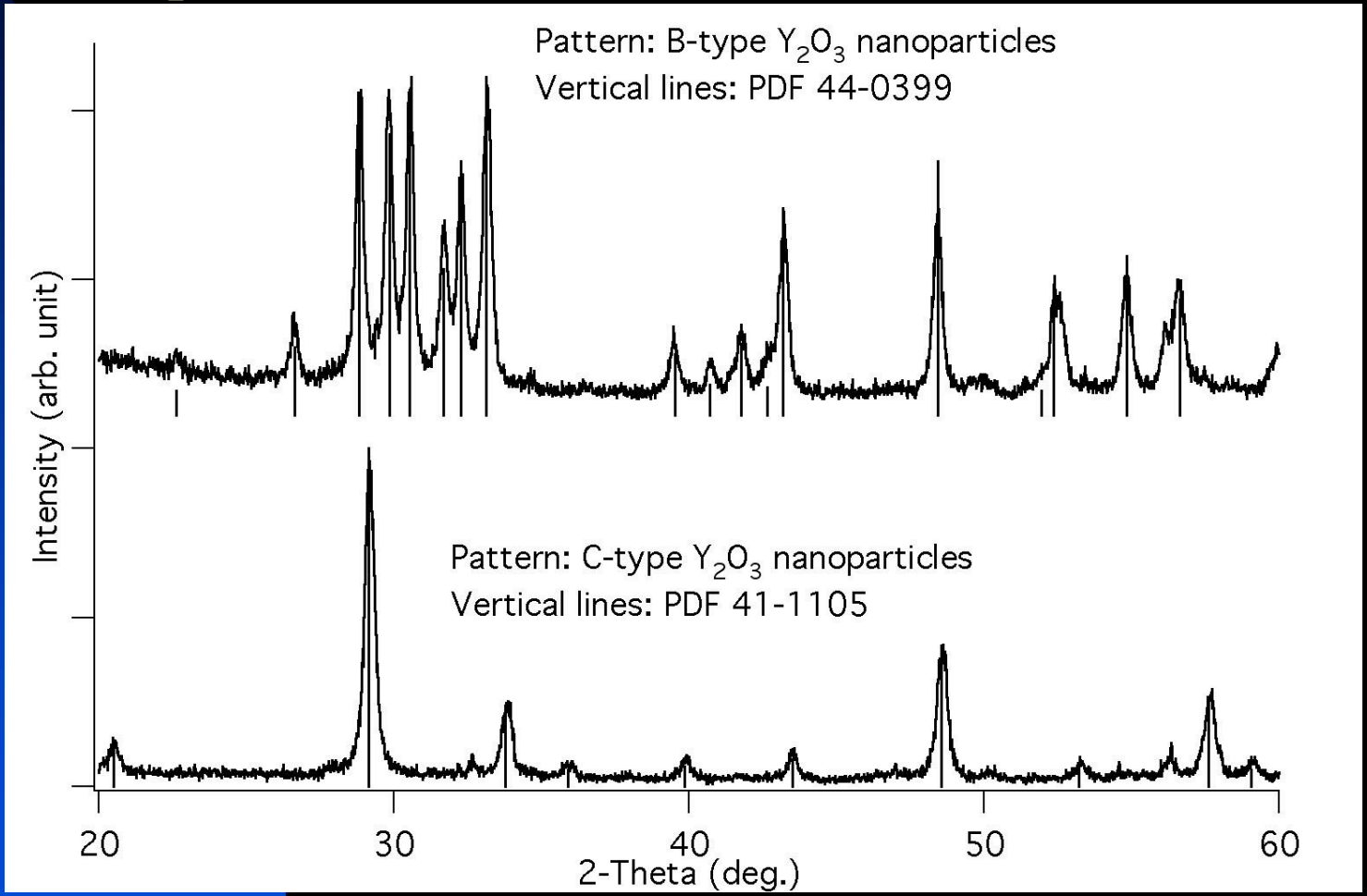
GaN QD in Block Co-Polymers (TEM)



Nanoparticles of RE oxides by Flame Synthesis



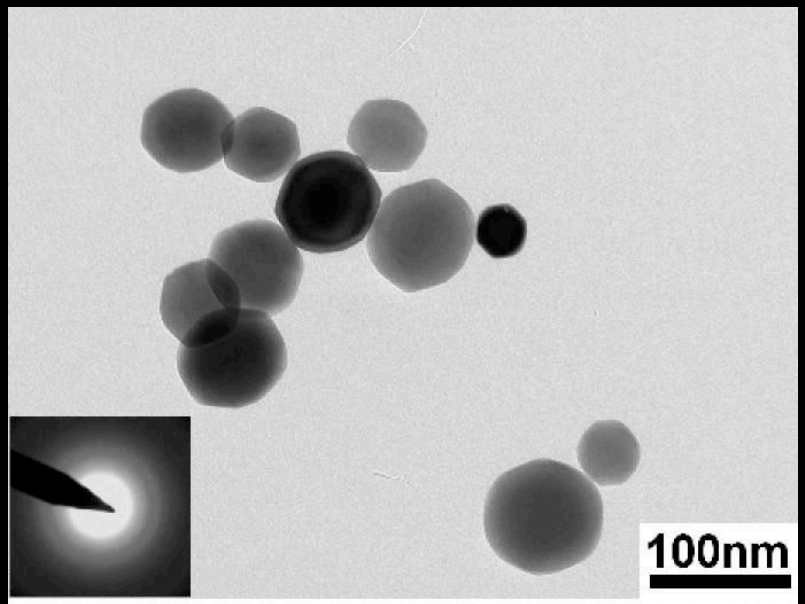
XRD of Yttrium Oxide Nanoparticles

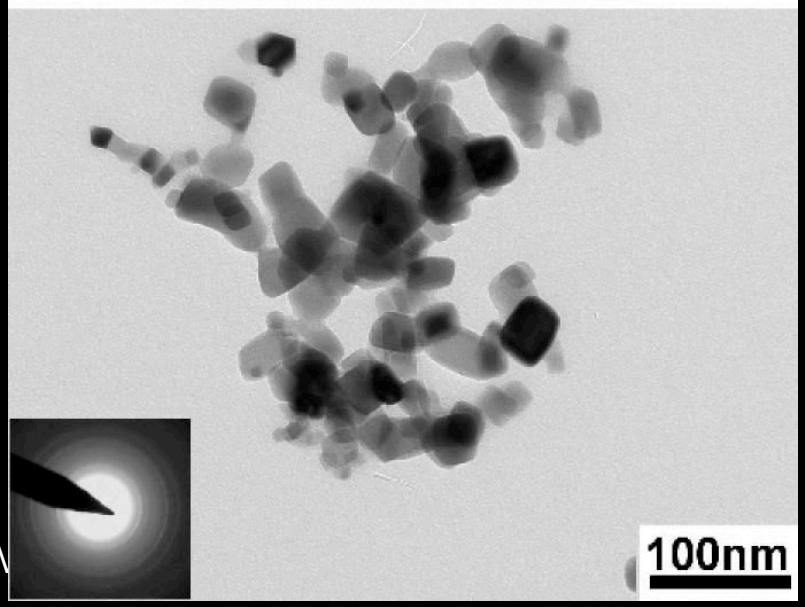


TEM/EELS of RE Oxide Nanoparticles

- Transmission electron microscopy and electron energy loss spectroscopy
- (EELS) used to distinguish structural details for the cubic and uncommon monoclinic crystal phases of heavy metal rare earth oxide nanoparticles
- Specifically, we systematically examined the EELS oxygen K edge for Ho, Tm, Er, and Yb sesquioxides in both phases

TEM of Yttrium Oxide Nanoparticles





EELS Results: RE Nanoparticles

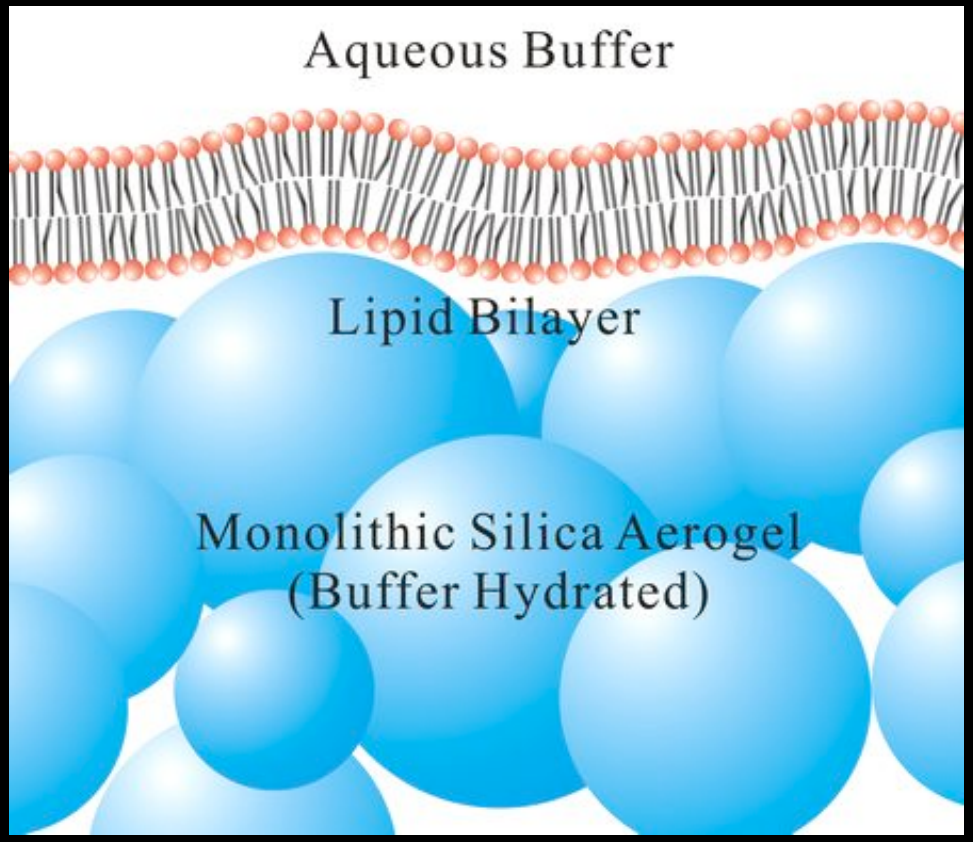
- We observed the usual double-peak structure of the oxygen K edge typically seen for oxygen atoms tetrahedrally surrounded by metal atoms, however we found the details of the energy loss near-edge structure to differ substantially between the two phases
- Our results indicate a greater peak separation for the cubic than for the monoclinic phase
- Furthermore, a trend of increasing peak separation with increasing atomic number was also noted for both phases in the series of rare earth oxide nanoparticles

RE Oxide Nanoparticles

- We have shown that the shape of the oxygen K edge and the energy difference between the two peaks observed in the EELS spectrum fine structure can be used to differentiate the cubic structure from the monoclinic in heavy RE2O3 NPs.

- We also show that, within the group of heavy REO samples we have examined, there is a trend in the degree of separation between the two oxygen K-edge peaks with respect to the RE ionic radii or atomic number.

Membranes Supported on Aerogels

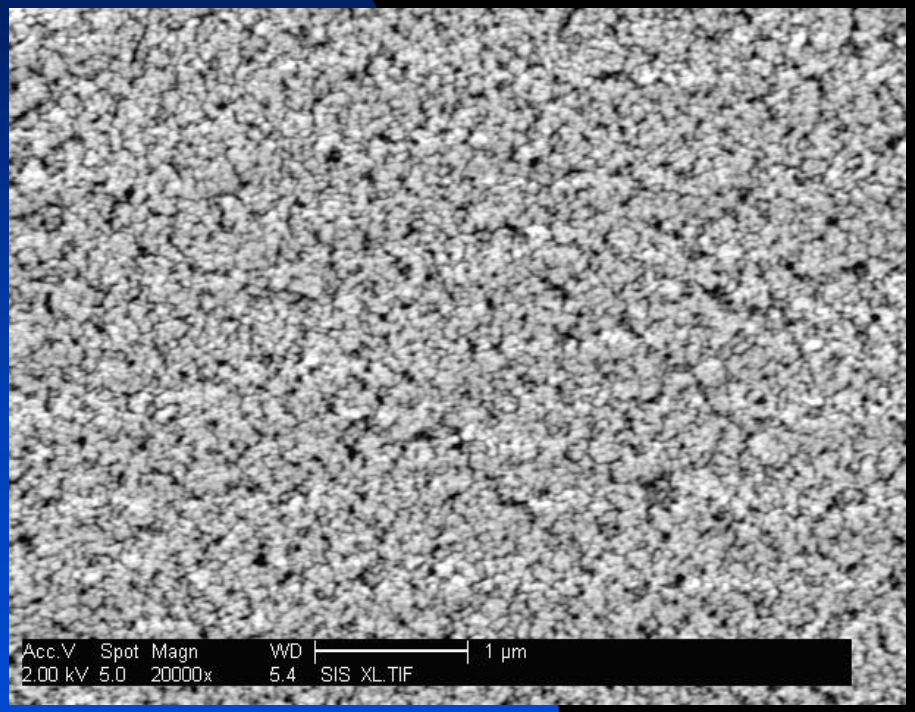


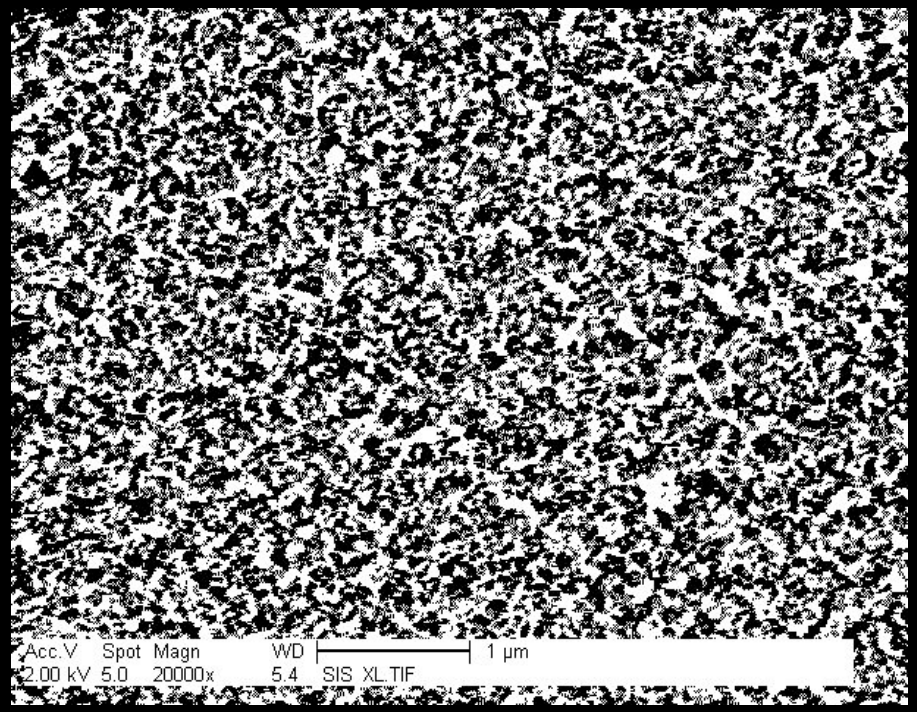
Potential benefits:
Integral protein accommodation, membrane transport studies, access to both sides of the membranes, flexibility of aerogel compositions

SEM of Aerogel Surface

SEM images show highly interconnected, nanosized pores and pearl string structure of silica beads of ~ 5-25 nm

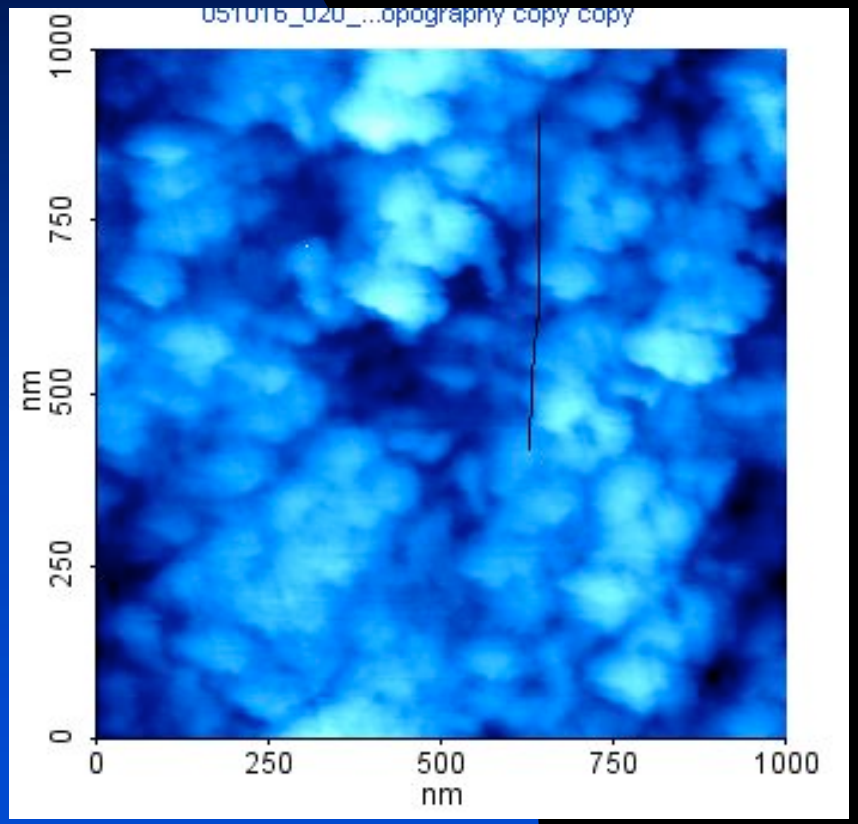
Left: original SEM image; Right: binary enhanced contrast

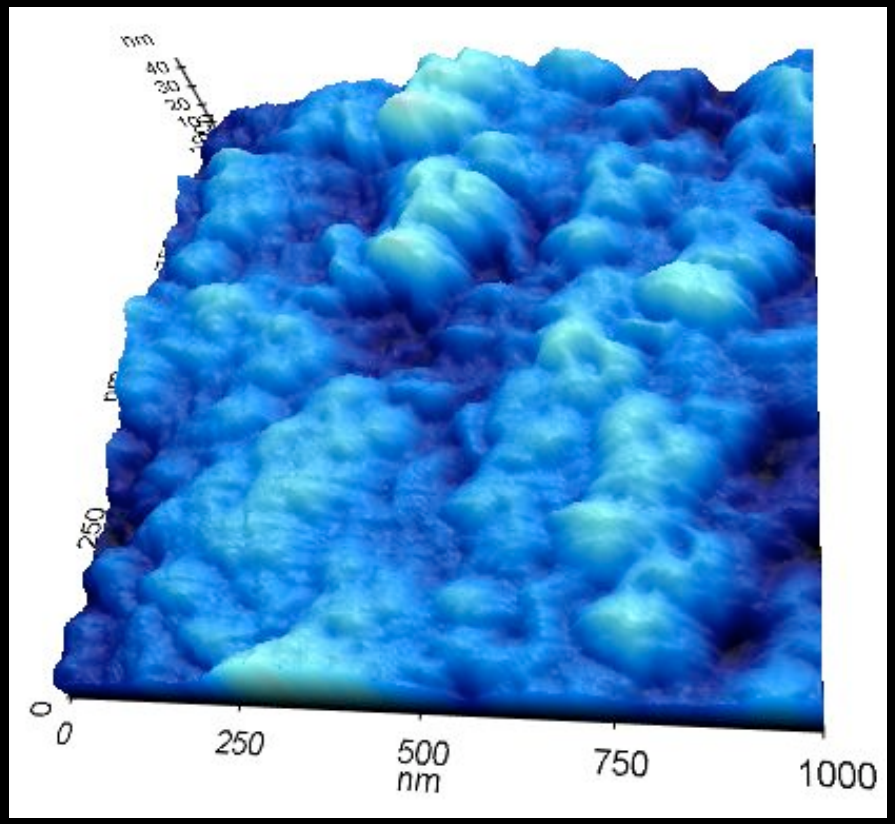




Au-Pd coated aerogel surface

Silica aerogel surface AFM



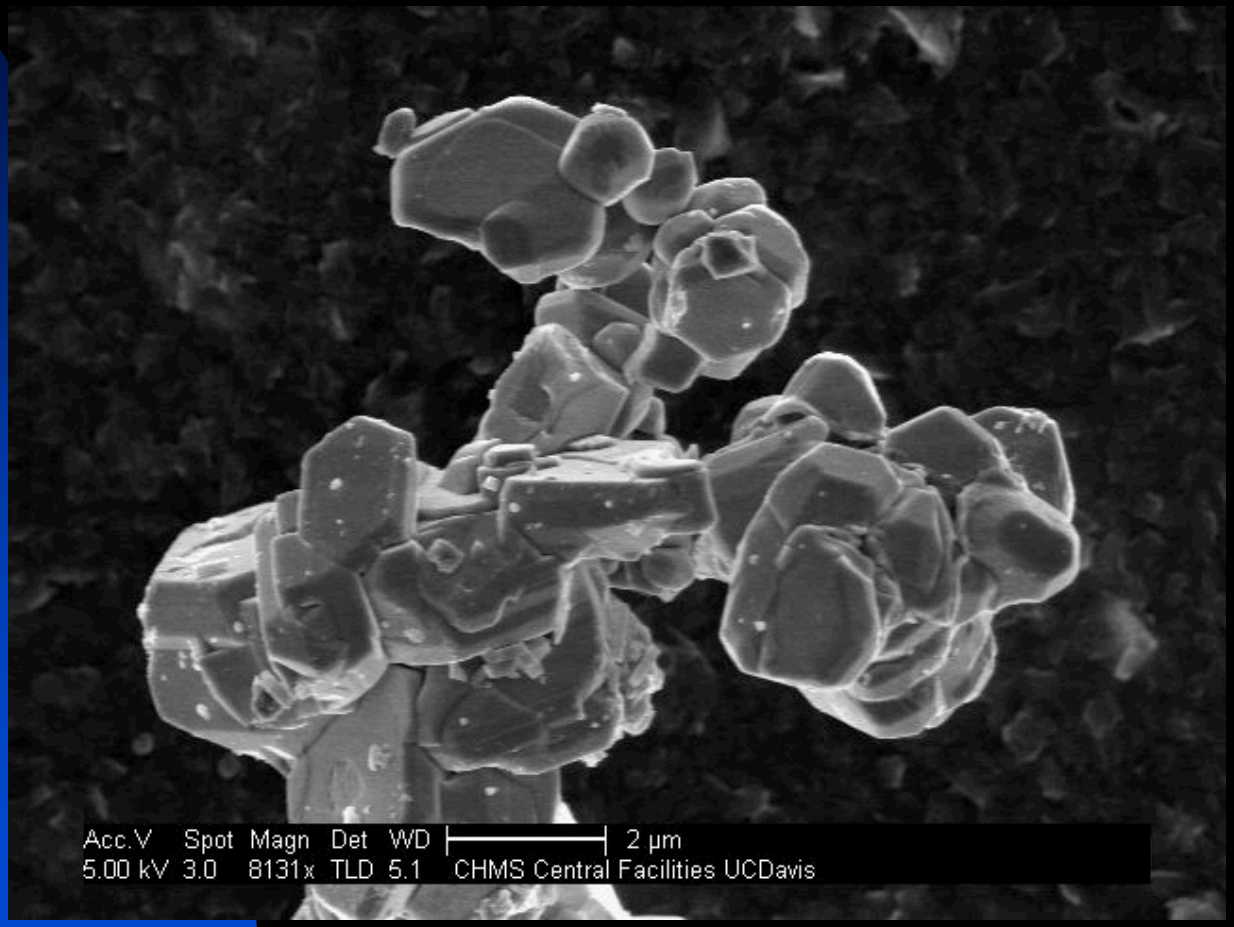


3-D Imaging of Nanomaterials Using Coherent X-rays

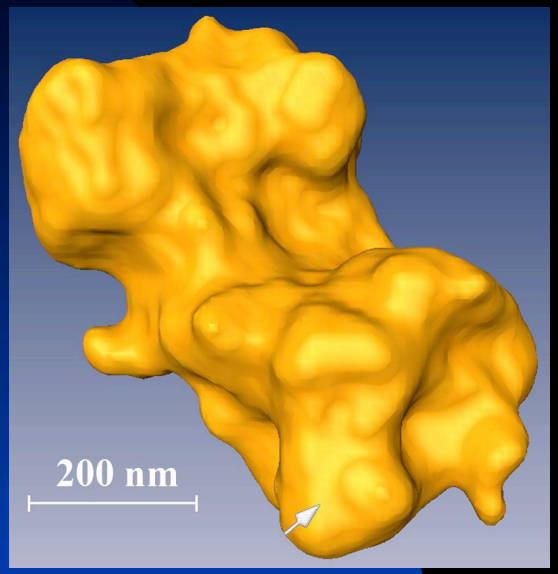
- By using coherent X-rays from a 3rd generation undulator beamline and newly developed 3D image reconstruction algorithms, we performed non-destructive 3D imaging of heat-treated GaN quantum dots particle at the nanometer resolution

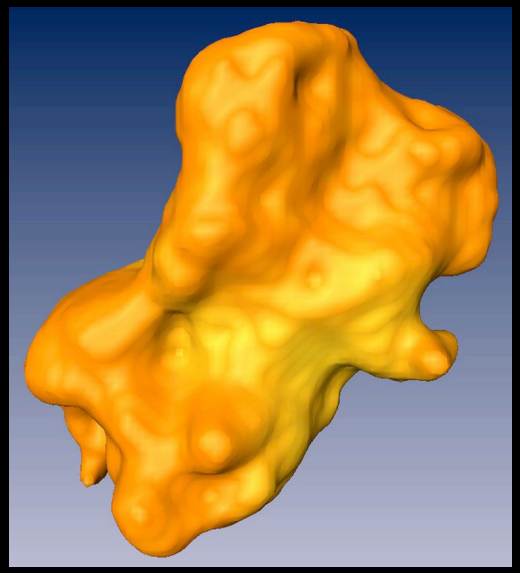
- We observed the platelet structures of the GaN quantum dots and the formation of small islands on the surface of the particle due to surface oxidization

GaN nanoparticle aggregates



Iso-surface rendering of a reconstructed 3D GaN quantum dot particle, showing:





(A) the front view (B) the side view (C) the back view

The GaN particle was heat treated under N_2 at 900°C for 24 h. The platelet structures of the GaN quantum dots are clearly visible. Small islands were formed on the surface of the particles due to surface oxidation.

3-D Imaging: Potential

- The ability to image the internal pore structures in three dimensions coupled with computational methods such as molecular dynamics and *ab initio* calculations is a major new directions with impact in many areas of chemical and materials sciences

3-D Imaging (cont'd)

- By sectioning the GaN particles cluster, slice by slice, each slice corresponding to 17 nm thickness, we determined the 3D distribution of GaN and β-Ga2O3 and confirmed the GaN-Ga2O3 core shell structures

- Unlike scanning transmission electron microscopy and electron diffraction, coherent X-ray diffraction microscopy does not have multiple scattering effects and can study a variety of materials with varied thicknesses.

Future opportunities

- 3-D coherent diffraction imaging of nanostructures is a powerful new structural characterization tool that will make a major impact on development of new materials

- Challenges in nanoscale materials include:

- ***core shell nanoparticles for light emission,***
- ***quantum dots in glass microspheres,***
- ***biomolecules assembled in and on aerogel surfaces***

Acknowledgments

Support for Research

- NSF-DMR Award 0444257(Ceramics Program)
- NSF-NIRT Award 0506602 (Biotechnology)
- Dept of Energy (LLNL-SEGRF Program)
- CPIMA (NSF MRSEC): Stanford-UC Davis-IBM