Nanoengineering — Toward Controlled Creation of New Inorganic and Composite Material Nanostructures

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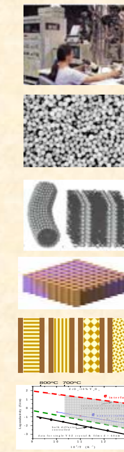
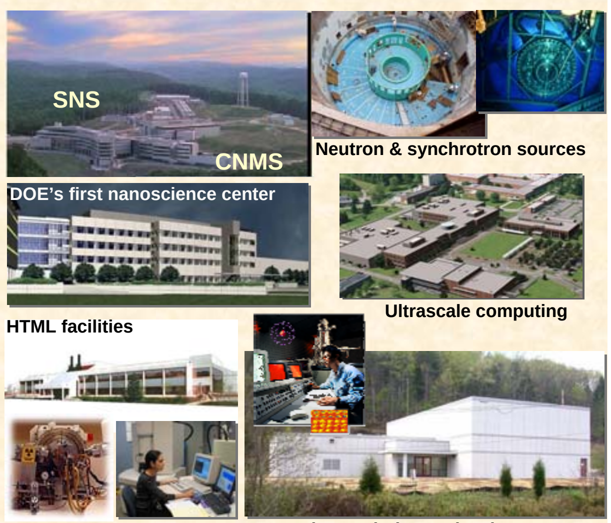
Outline

- **General introduction**
  - Our interests and facilities in nanomaterials
  - Nanoengineering
- **Chemical engineering of nanoparticles and material nanostructures**
  - Liquid phase synthesis
  - Processing by external fields
- **"Molecular engineering" of nanostructures**
  - Arrays of inorganic nanochannels/nanotubes: orientation/ordering control
  - Space-confined self-assembly: nanostructure control within inorganic nanowires
- **Potential applications**
  - Fuel cells, solar cells, sensors, …
- **Concluding remarks**



ORNL Is A World Leader in Nanosciences and Nation's Premier Facilities in Advanced Materials Research

- Center for Nanophase Materials Sciences (CNMS)
- Spallation Neutron Source (SNS) & High Flux Isotope Reactor (HFIR) scattering facilities
- High-Temperature Materials Laboratory Facilities (HTML)
- (NEW!) Center for Radiation Detection Materials and Systems (CRDMS)



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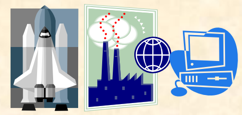
Engineering vs. Science

- Definition (per Webster's):
  - **Science**: "a branch of knowledge or study dealing with a body of facts or truths systematically arranged and showing the operation of general laws … systematic knowledge of the physical or material world …"
  - **Engineering**: the art or science of making practical application of the knowledge of pure sciences, as physics, chemistry, biology, etc. …
  - **Nanoengineering**: ???
    - Must be enabling, not just the scale-up problem
    - Beyond existing chemical engineering, materials engineering, etc.
    - Need a transition from nanoscale science to nanoengineering



NanoTechnology shall go beyond NanoScience !
- Process scale
- Level of precision of process control
- Production through-put rate
- Dimension of products

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Our Interests: Develop "NanoEngineering" for Controlled Nanosize & Nanostructure

- **Chemical processes** (including biomimetic processes)
  - "bottom-up" in nature
  - suitable for large-scale production economically
- **Engineered Chemical Processing** of nanomaterials – a new paradigm
  - Nanoscale chemical reaction and process engineering (chemical engineering)
  - Molecular engineering (chemistry + self-assembly)
  - Interface engineering

Process Engineering At Nanoscale

Scalable processing with nanoscale process control ↓ *(beyond today's nanosciences and engineerings)*

Controlled or Large-Scale Formation or Assembly of Designed Nanostructure

↓

Controlled Properties/Functions

Molecular Design and Process Engineering Control the Growth of Nanostructure

examples of fundamental building blocks

Particle
Size & distribution
Shape
Crystallinity
Surface chemistry
Pore structure
Core-shell
Colloidal crystal
Linked network

Film uniformity
Located growth on surface
Nanophase grain size
Surface roughness
Crystal structure
Patterned film
Film porosity
Multilayer

Porous inorganics
Nanopore size
Shape
Orientation
Domain scale
Nanorod,wires
Nanocomposites

Chemical process understanding and control must be obtained to achieve nanoscale engineered build-up of materials

Nucleation and Growth Is An Enabling Approach to Build Up Advanced Nanomaterials

- Allow *bottom-up* manufacturing via nucleation and growth
- A world of inorganic materials can be made by controlled "living growth"

"Controlled" build-up (growth) of nanophase/particles/nanopores

Homogeneous ↓ *Heterogeneous*

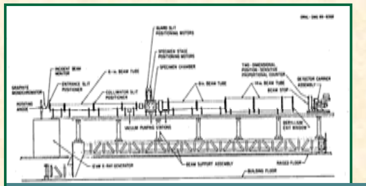
Tailored nanostructures in advanced materials

Engineered manufacturing of advanced ceramics/composites could impact various applications

- Energy storage and conversion (fuel cells, solar cells)
- Separations (inorganic membranes)
- Catalysis
- Micro-/nano-electronics
- Sensors, devices
- Targeted therapy, drug delivery, etc.

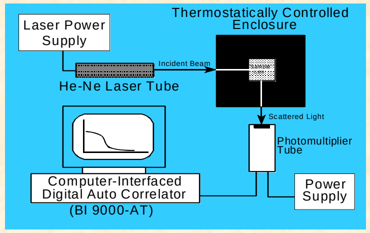
We Focus on Real-Time Process Monitoring and Control to understand & develop engineering processes for manufacturing nanomaterials

- **Small-Angle Scattering (SAXS and SANS)** *(0.2 – 200 nm length scale for SAXS)*



$I(Q) = I_e(Q) N_p (\Delta\rho v)^2 \exp(-Q^2 R_g^2/3)$

- **Dynamic Light Scattering (DLS)** *(5 – 1000 nm nanosize range)*



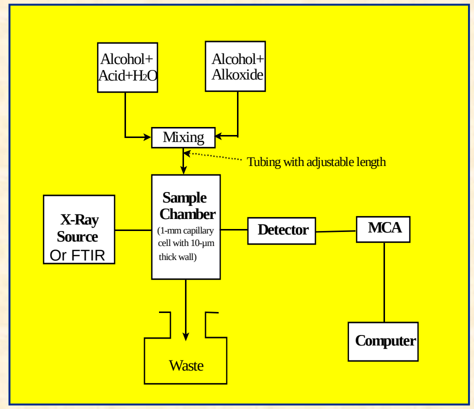
- **In-situ, high-temperature XRD (HTXRD)**

HTML facility offer existing capability

Scattering is complementary to electron microscopy **HRTEM**

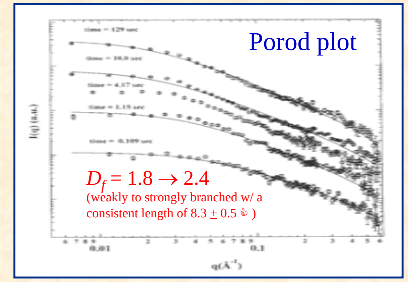
Example: SAXS Monitoring of Sol-Gel Processing of Nanomaterials in Solutions

We have developed capability for studying early stages (as short as 80 ms).



A "Steady-State" Technique Based on Rapid Mixing Flow-Cell

SAXS from Early-Stage Zr-Nanoclusters



Mass fractal scattering model

$I(q) = NP(q)\,S(q)$

N = number density

Form factor (for spherical particles): $P(q) = V^2(\Delta\rho)^2\{3[\sin(qr_0) - qr_0\cos(qr_0)]/(qr_0)^3\}^2$

Structure factor: $S(q) = [1+1/(qr_0)^{D_f} D_f \Gamma(D_f-1)\sin[(D_f-1)\arctan(q\xi)]/[1+1/(q^2\xi^2)]^{(D_f-1)/2}$

J. Mater. Sci., 35, 1957 (2000).
J. Non-Crystal. Solid, 246, 197 (1999).

Outline

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- Molecular "engineering" of nanostructures
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  - Space-confined self-assembly: nanostructure control within nanowires
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  - Fuel cells, solar cells, sensors, …
- Concluding Remarks

Example: Engineered Processes Need to be Developed for Novel DTS Processing of Monodispersed Oxides

Highlight of Dielectric-Tuning Synthesis (DTS)

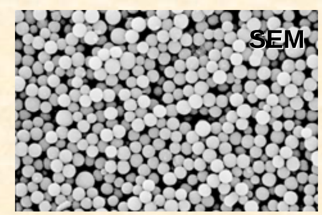
Journal Cover for Our $BaTiO_3$ Work

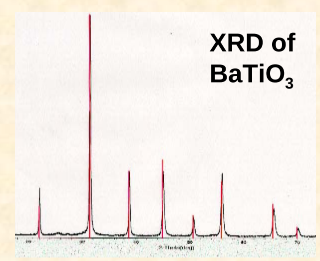
J. Colloid Inter. Sci.,222, 20 (2000).
J. Amer. Ceram. Soc., 82, 2313 (1999).

Oxides: e.g. ZrO_2, TiO_2, $BaTiO_3$, and $ZrTiO_4$

Uniqueness:
- use inorganic precursors
- low temperature synthesis
- different from sol-gel method
- Capable of sol-gel processing

Features:
- **Size:** near-monodispersed
- **Phase:** nanocrystalline or amorphous
- **High purity**
- **Nanoscale homogeneity**
- **Controllable morphology**





J. Mater. Sci. 35, 1 (2000).
Powder Technol., 110, 2 (2000).

Scale-up of DTS chemical process for nanoparticle synthesis

- **Investigate engineering science issues: scale up, transition to continuous production**

Glass vials (10-50mL)

↓

Engineering reactors (5000mL, better control in T, P, mixing parameters)

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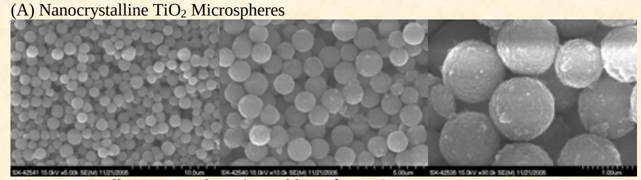
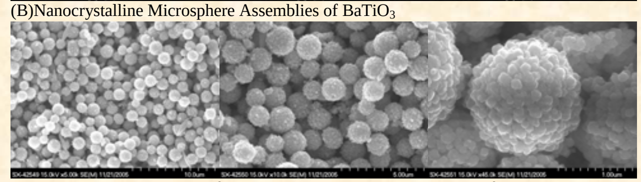
Technology for engineering scale production of nano-particles are still being developed for future energy generation and storage

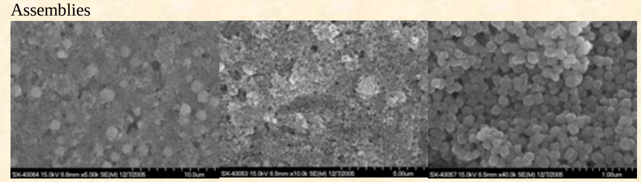
(A) Nanocrystalline TiO_2 Microspheres



(B)Nanocrystalline Microsphere Assemblies of $BaTiO_3$



(C) Dispersed Nanocrystals of $BaTiO_3$ by Designed Dis-aggregation from Microsphere Assemblies



New Arenas: Engineering Control of the Size and Nanostructures

Current nanoscience effort is restrained inside this box → Chemistry, materials science and engineering, etc.

"Outside-the-Box":

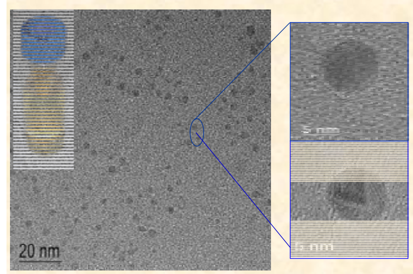
"engineered" monitoring and control of <u>processes</u>

- **Laser-assisted processing**
- **Field-directed processing** (Electrical, Magnetic, Microwave…)
- **Electrochemical processing**
- **Thermal processing**
- **Molecular assembly-assisted processing**

Diversified physical/chemical <u>means of engineering controls</u> enable
- novel ways of manufacturing
- creation of new nanostructures
- better control of process parameters

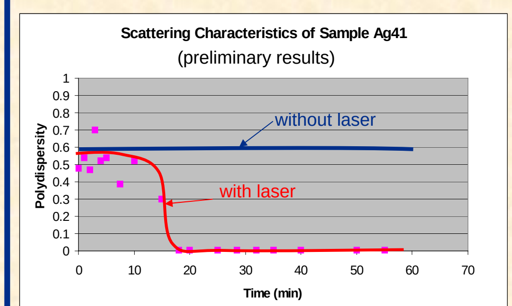
Laser Processing: Induced Nanocrystal Homogenization

"Naked" Metallic Nanocrystals by A *Thermal Electrochemical Process*



This process, developed at ORNL, generates possibly a new class of Ag nanocrystals.
- **Size < 10 nm**
- **Free from any organic capping molecules**
- **Colloidally stable**

2 orders-of-magnitude reduction in polydispersity! (from 0.5 to 0.005) while size does not change

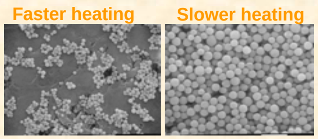


<u>Polydispersity</u>: a parameter in dynamic light scattering measurement to quantify particle size distribution.
- < 0.02, for monodisperse or nearly monodisperse samples
- 0.02-0.08, for narrow size distributions
- > 0.08, for broader distribution

Field-Coupled Chemical Processing

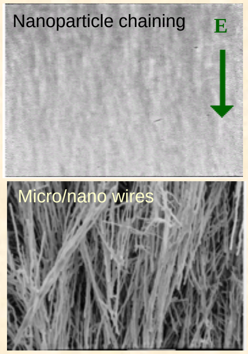
(Engineered Tailoring of Nanocluster Growth/Assembly Needs More R&D)

Programmable Microwave Hydrothermal Reactions



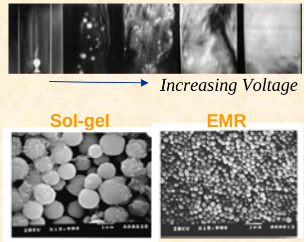
- Microwave volumetric heating **overcomes *heat transfer* limitations**
- Particle size can be controlled by manipulating the nucleation rate
- Achieving computer programmed synthesis

Growth of Microfibrils in Electric Field



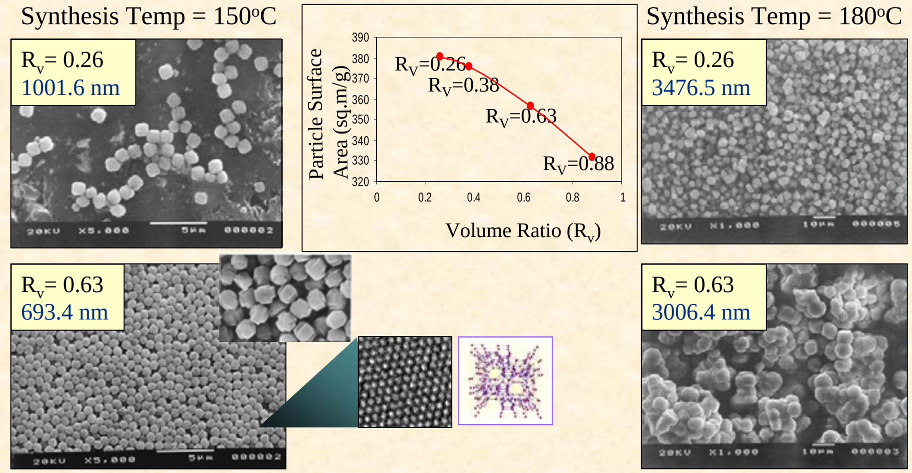
- field induce polarization and **oriented growth**
- Inorganic long "hair":
  - morphology/diameter can be tailored

Electrohydrodynamic Mixing Reactor (EMR)



- Improved nanoscale mixing **overcomes *mass transfer* limitations**; allows
  - –greater control of nucleation
  - –synthesis beyond sol-gel processing limit

Microwave Processing Offers More Flexibility than Conventional Hydrothermal Processing



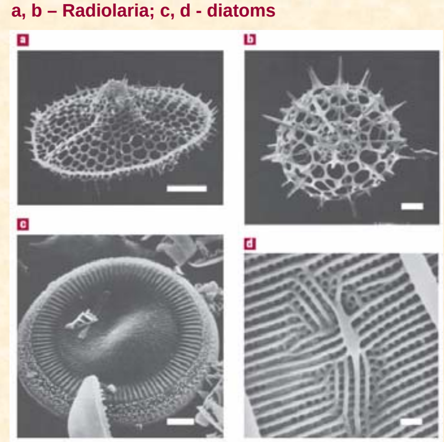
Various changes in zeolite particle size and morphology can be realized.

Outline

- General introduction
  - ORNL nanoscience, research facilities, etc.
  - Our research interests and expertise
- Liquid-phase synthesis of nanoparticles
- Processing engineering of material nanostructures
- **Molecular "engineering" of inorganic nanostructures – a new paradigm**
  - Array of nanochannels/nanotubes: orientation/ordering control
  - Space-confined self-assembly: nanostructure control within nanowires
- Potential Applications
  - Fuel cells, solar cells, sensors, …
- Concluding Remarks

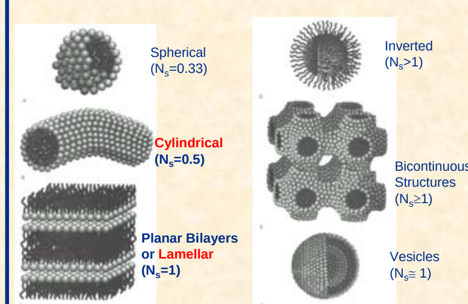
Natural Beauty and Diversity of Self-Assembled Nanomaterials

Silicic skeletons of unicellular organisms: a, b – Radiolaria; c, d - diatoms



Sanchez et al., Nature Mater. 2005

Molecular self-assembly is the spontaneous and reversible organization of building-blocks (molecules) under thermodynamic equilibrium conditions into structurally well-defined and rather stable arrangements through a number of noncovalent interactions. (Shuguang Zhang 2002, Tirrell & Katz 2005)

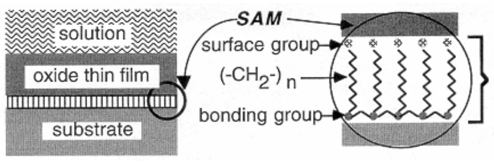


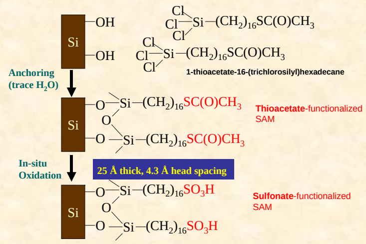
Hiemenz, Principles of Colloid and Interfacial Sciences

- **Biomimetism/bioinspiration → Design/creation of innovative materials/systems**

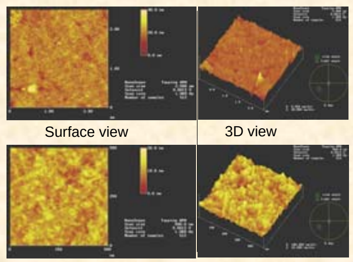
Molecular Design-Based Surface Deposition and Interface Film Growth of Oxides

- Modify substrate with organic self-assembled monolayers (SAM)
- Chemical solution deposition of inorganic layer on SAM





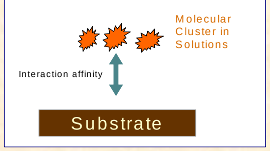
- *Inter. J. Appl. Ceram. Technol.*, April (2004)
- *Solid State Ionics*, 151, 69 (2002).



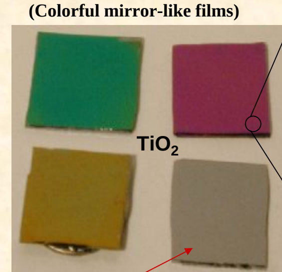
- Important for film growth and interface engineering in nanocomosites
- We have grown and studied various oxide deposition (ZrO_2, HfO_2, etc.)
- The approach has induced homogeneous deposition and improved
  - uniformity, roughness
  - coherence, adherence
  - possible selective deposition

Chemical Processing May Control Thickness and Nanostructure of TiO_2 Film

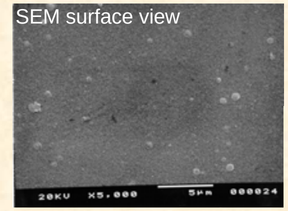
Strategy:
Design of Molecular Complex
Ti Species or Nanoclusters
in Bulk Solutions

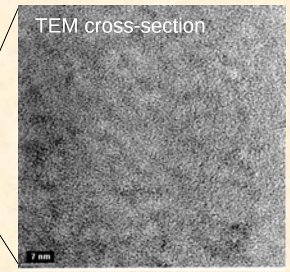


(Colorful mirror-like films)

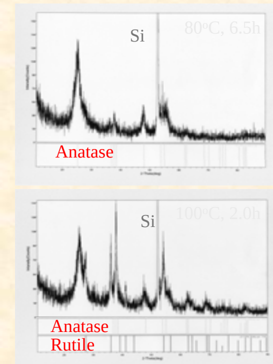


Control (Bare Si Wafer)



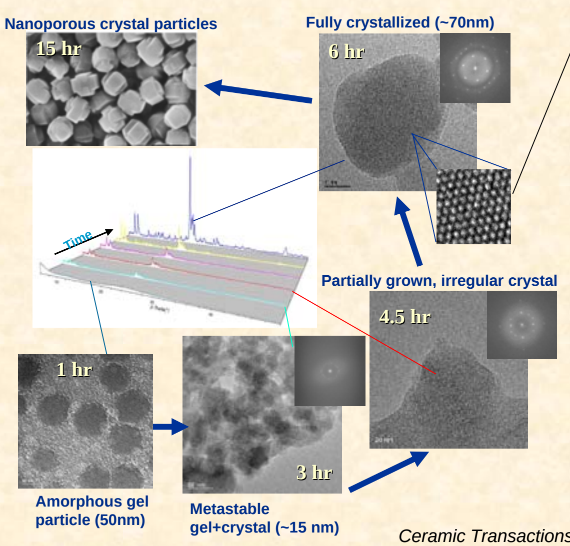


Application to Solar Cells?



- Nanocrystalline TiO_2 films (containing ~3 nm nanocrystals)
  - high refractive index (2.2)
  - large band-gap (up to 3.7 eV)
  - low surface roughness

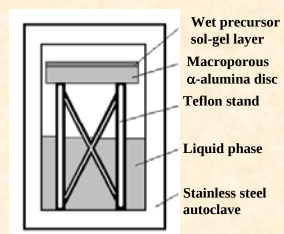
Molecular-Templated Growth and Crystallization of Zeolite Particles

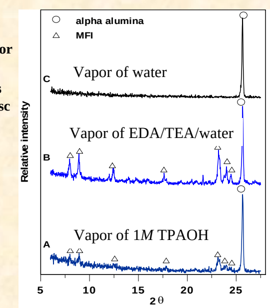


- A good model system for understanding large-scale process but with possible achievement of nanoscale homogeneity
  - Sub-nm micropores are created by molecular templating inside a crystal particle
  - Small template molecules control the size, shape, and uniformity of the pores
- Still needs further development for efficiency, selectivity, and cost saving for practical applications in catalysts and adsorbents

Ceramic Transactions, 137, 3-21 (2003).

A Novel Vapor-Phase Thermal Conversion Synthesis of MFI Zeolite Membranes

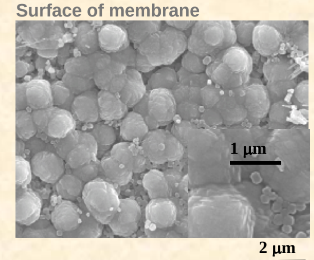




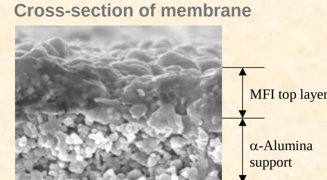
Results of zeolite membrane synthesis under different conditions.

Synthesis sol-gel on substrate	Liquid phase	Top layer	Thickness (μm)	Quality
7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	1 M TPAOH	MFI	3	Good
7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	EDA/TEA/H_2O (8.1/30.7/61.2)	MFI	12	Poor
7.0% SiO_2 + 2.1% TPAOH + 0.8% NaOH + 90.1% H_2O	H_2O	Amorphous	---	---
7.0% SiO_2 + 2.9% NaOH + 90.1% H_2O	1 M TPAOH	NaP-cubic	---	---
7.0% SiO_2 + 2.9% NaOH + 90.1% H_2O	EDA/TEA/H_2O (8.1/30.7/61.2)	ANA-cubic	---	---

Surface of membrane



Cross-section of membrane



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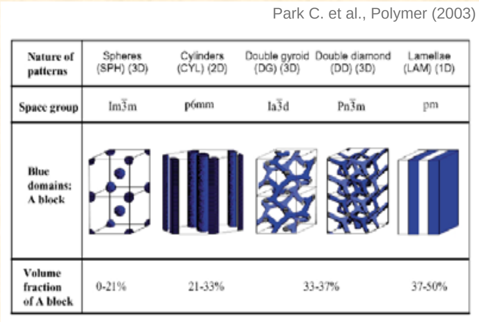
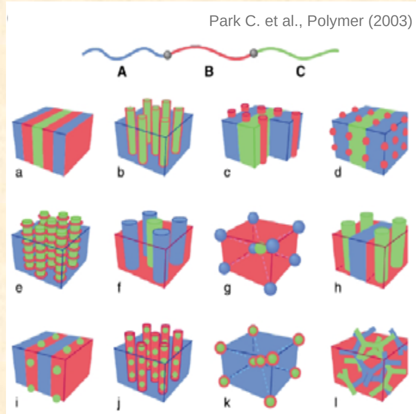
J. Mater. Sci., 38 (5): 979 (2003).

Rich Morphologies via Self Assembly and Organization



Schematic phase diagram showing the various "classical" BCP morphologies adopted by non-crystalline linear diblock copolymer. The blue component represents the minority phase and the matrix, majority phase surounds it.



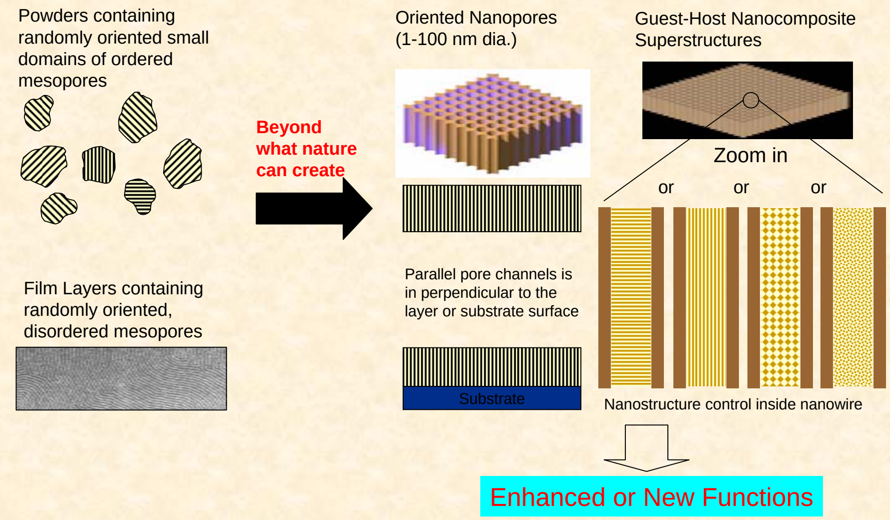
Schematic of morphologies for linear ABC triblock copolymer. A combination of block sequence (ABC, ACB, BAC), composition and block molecular weights provides an enormous parameter space for the creation of new morphologies. Microdomains are colored as shown by the copolymer strand at the top, with monomer types A, B, and C confined to regions colored blue, red, and green, respectively.

- **Polymorph selection in porous block copolymers**
  Ward, Hillmyer, J. Am. Chem. Soc., 126, 3382 (2004)
- **Tailored pore wall functionality**
  Hillmyer et al., Macromolecules, 38, 3 (2005)
  ibid, Faraday Disc. 128, 149 (2005)

Molecular Self-Assembly Processing of Inorganic Nanomaterials -- Grand Challenges

(a) Current state of the art in molecular templated synthesis

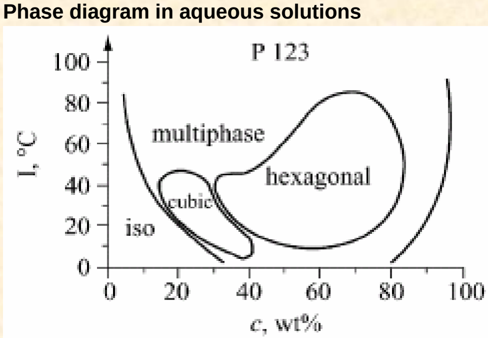
(b) Future realization of large-scale ordering and control of orientation and wall function



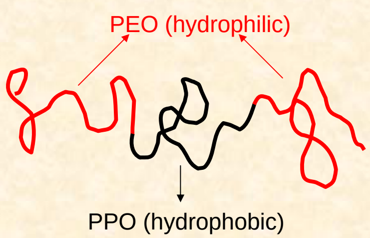
Self-Assembly of P123

P123: $(PEO)_{20}(PPO)_{70}(PEO)_{20}$

Phase diagram in aqueous solutions



Wanka G. et al., Macromolecules 27, 4145 (1994).

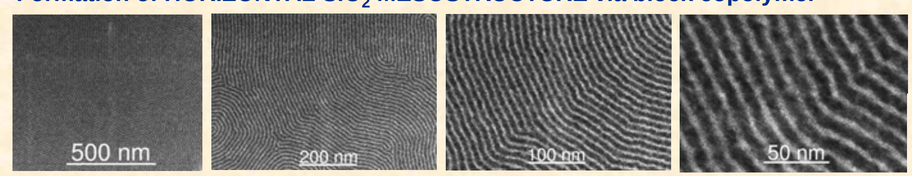


Hydrophobic effect in dilute aqueous solution causes the self-assembly

Molecular Design-Based Build-up

Developing Hybrid Molecular Self-Assembly of Oxide Mesostructures

Formation of HORIZONTAL SiO_2 MESOSTRUCTURE via block copolymer



Z-contrast STEM images: Bright region representing silica. Channels (**7.5-nm gap**) exhibit a highly connected horizontal structure. (V. F. de Almeida, D. A. Blom, L. F. Allard, M. Z. Hu, S. Dai, C. Tsouris, Z. Zhang, Microscopy and Microanalysis 2003, San Antonio, Texas, August 3-7, 2003.)

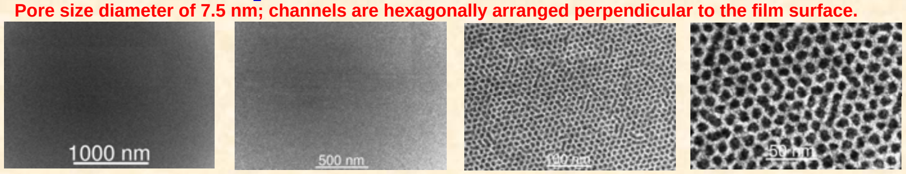
Key Issues:
- **Orientation control: let meso-channels standing up normal to substrate?**
- **Expanding domain size of ordering**
- **Structure stability**

Molecular Engineering-Based Build-up

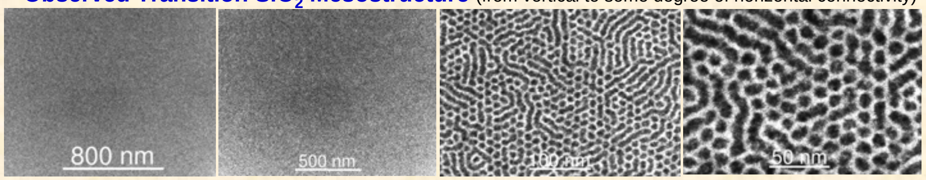
Process Engineering Enables Channel <u>Orientation</u> in Nano/Mesoporous Films

•Achieved Vertical SiO_2 Mesostructure (black dots are channel pores, bright region-SiO_2)

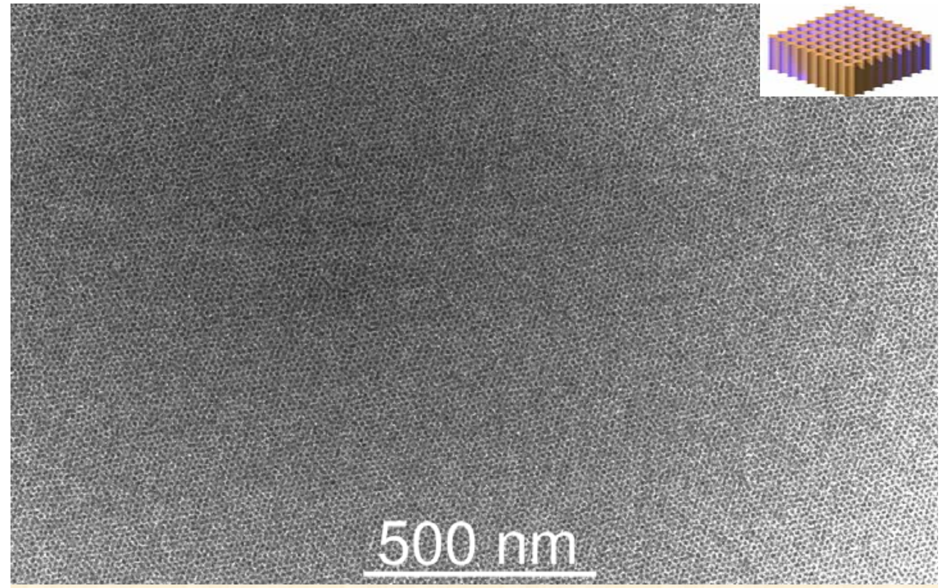
Pore size diameter of 7.5 nm; channels are hexagonally arranged perpendicular to the film surface.



•Observed Transition SiO_2 Mesostructure (from vertical to some degree of horizontal connectivity)



But, the engineering sciences (that control the mechanisms of channel orientation, control of aspect ratio and pore connectivity, ordering scale-up, etc.) still need to be developed !

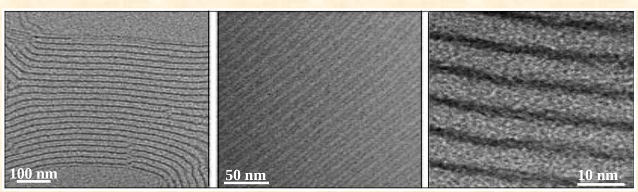


- **Very large area of hexagonal ordering: achieved mm range**
- **Possible hard template for arrays of nanoscale vertical channel columns**
- **Many potential applications (fuel cells, solar cells, sensors, catalysts, etc.)**

Molecular Design-Based Build-up

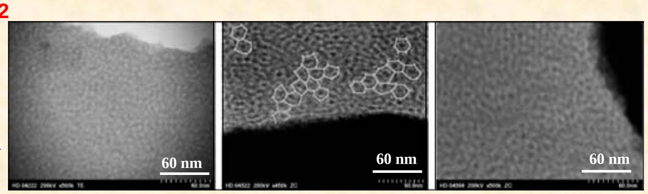
Understanding Controlled Self-Assembly: Mesopore Orientation in Many Other Oxides

High-resolution TEM images of titania layer mesostructures containing **parallel pore channels with spacing of ~10nm. Dark pore channel lines correspond to titania phase.**



TiO_2

STEM images of mesostructured titania showing **distorted hexagonal phases** (*TE*-transmission mode; *ZC* – Z-contrast mode, brighter areas correspond to titania phase).



(Hu, unpublished results)

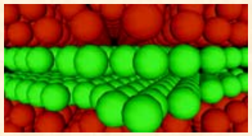
Nano-in-Nano Control: Space-Confined Self-Assembly of Organic-Inorganic Wires in Nanopore Channels (0.5 – 200nm)

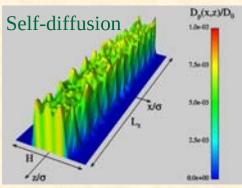
Self Assembly in Confined Pore Channels: Guest-Host Superstructures

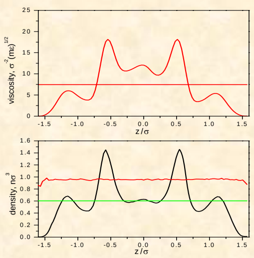
Potential Applications

Electronic materials, Fuel-cell electrolyte, Optical materials, Magnetism, Catalysts, Nanocomposites

Results from Statistical Mechanical Theory and EMD simulation

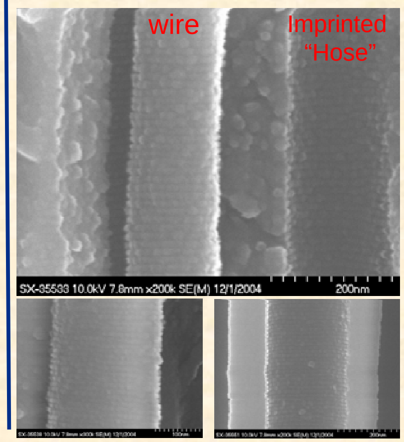




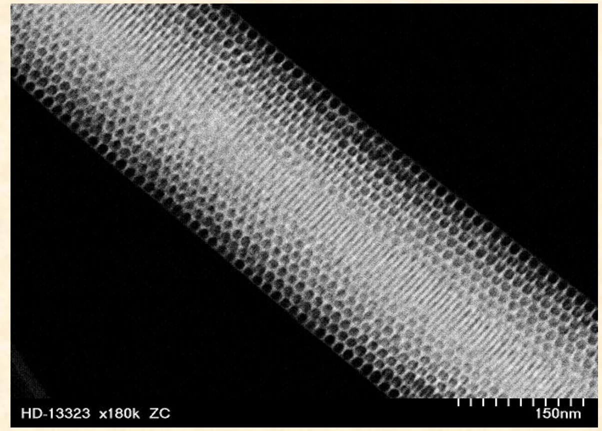


J. Nanosci. Nanotechnol. **2**, 209 (2002).
Ceram. Trans. **137**, 101 (2002).

- **Wires inside pore channels consist of <u>oriented, parallel stacked layers</u> of oxide (10-nm thick)**



Revealing "layered" structure with STEM

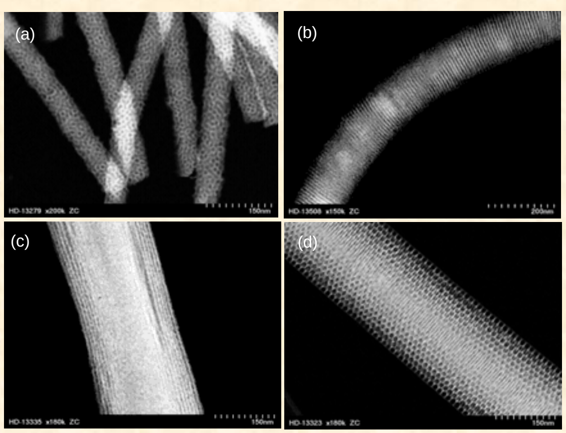


"Layered" nanostructure (SEM)

↓

highly oriented and ordered hexagonal mesophases (STEM)

Molecular & Process Engineering Approach Could Enable Refined "Nano-in-Nano" Control of Nanostructures



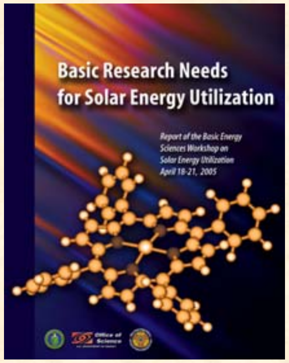
Various oriented and ordered inorganic oxide nanostructures inside space-confined wires/channels:

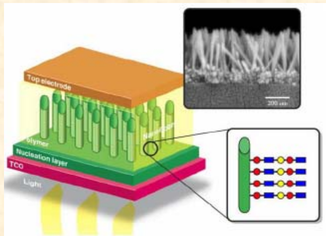
(a) Random oriented mesopores and small domain size of hexagonal phases,
(b) Parallel lamellar phase oriented in perpendicular to the pore channel,
(c) Lamellar phase oriented in parallel to the pore channel,
(d) Highly ordered and oriented hexagonal mesopores (7.5nm dia.).

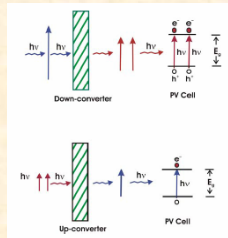
Outline

- General introduction
  - ORNL nanoscience, research facilities, etc.
  - Our research interests and expertise
- Liquid-phase synthesis of nanoparticles
- Processing engineering of material nanostructures
- Molecular "engineering" of nanostructures
  - Array of nanochannels/nanotubes: orientation/ordering control
  - Space-confined self-assembly: nanostructure control within nanowires
- **Potential Applications**
  - Fuel cells, solar cells, sensors, …
- Concluding Remarks

Success Could Directly Impact Energy Materials of the Future: Fuel Cells and Solar Cells







Concluding Remarks

- **Chemical engineering and "molecular engineering" of nanosize and nanostructure are frontiers for new discovery and creation of innovative materials.**
  - **Chemical processing offers great opportunities in large-scale manufacturing and production while allowing control of material nanostructures and functions**
- **At ORNL, we endeavor to develop new engineering sciences and manufacturing capabilities in nanomaterials for energy, security, and other applications**
  - **Nanomaterials Engineering Laboratory: Focus on chemical processing and engineering**
  - **State-of-the-art instrument facilities on real-time process monitoring and nanoscale characterization (CNMS, SNS, …)**
- **Future nanofabrication demand "process understanding-based" control of**

  Size → Shape → Ordering → Orientation

Acknowledgments

Post-Docs: L. Pozhar, J. Dong, A. Singhal

Students: P. Lai, X. Wang, L. Khatri, J. Zielke, S. Morton, A. DeBaille, V. Kurian, G. Miller, K. Booth, B. Grant, J. Clavier

ORNL Colleagues: C. Easterly, D. DePaoli, R. Hunt, A. Payzant, J.-S. Lin, C. Rawn,. Allard, D. Blom, I. Anderson, G. Jellison, Y. Wei, P. Becher, T. Armstrong, C. Mattus, J. Wang, V. de Almeida

Collaborators: D.-L. Shi, M. T. Harris, D. Green, B. Lee, Y.-S. Lin, M. DeGuire, N. Xu

- Research sponsored by
  - **Division of Materials Sciences, Material Chemistry Program, Office of Sciences, U.S. Department of Energy (DOE)**
- ORNL HTML facility

Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725

Overview: Process Engineering and Molecular Engineering Enable Tailored Chemical Processing of Diversified Nanostructures