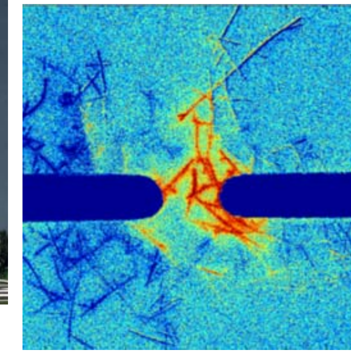

Functional Nanomaterials

Research Opportunities Using Neutron Scattering

Doug Lowndes

Scientific Director, CNMS

Contributors:

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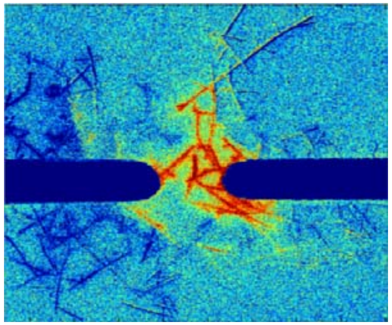
Nanomaterials and Neutrons Workshop
SNS-HFIR User Meeting
Oak Ridge National Laboratory
October 13, 2005

Functional Nanomaterials Theme Focuses on Central Nanoscience Challenges

[1] **HIGHLY CONTROLLED SYNTHESIS** of thin-film heterostructures and nanoscale materials

- *Artificially layered oxide structures*
  - Electric and magnetic properties result from nanoscale interactions
  - Atomic-layer control → systematically explore and tune
- *High quality nano- rods / wires / tubes and quantum dots*
  - Mainly oxides and carbon-based

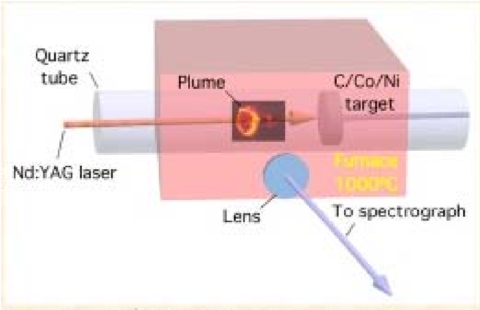


[2] **DEVELOP METHODS to USE NANOMATERIALS in FUNCTIONAL NANOCOMPOSITES AND DEVICES**

- Emphasis: Create novel or greatly enhanced properties
- Measurements and modeling to understand

[3] **Time-resolved, in situ spectroscopy and diagnostics of early stages of nanomaterials growth**

- Understand growth mechanisms → control synthesis



Advantages of Co-Location of CNMS and SNS

- **CNMS provides unique nanomaterials synthesis and processing capabilities**
- **SNS-HFIR provides unique measurement capabilities**

KEY OPPORTUNITY FOR DEVELOPMENT OF NEUTRON SCATTERING

Close integration of staff and facilities enables *the design of novel samples* as integral part of *planning* neutron scattering studies

EXAMPLES

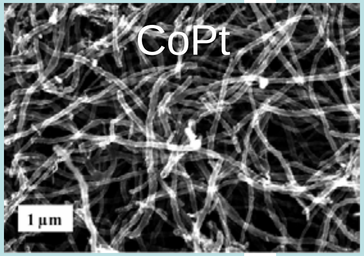
- ***High-yield*** **synthesis of functional nanoporous (and other) carbon- and oxide- nanomaterials for neutron scattering**
- **Growth of *thick* oxide heterostructures (artificially layered single crystals) for studies using *all* neutron methods**
  - **Reflectometry, diffraction, inelastic scattering**

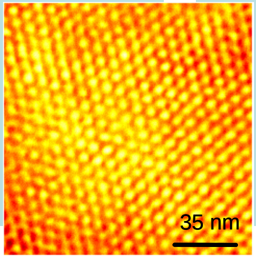
A CNMS Synergy of Co-Location

Functional Nanomaterials: High-Yield Nanomaterials Synthesis for Neutron Scattering

SNS provides unique opportunities

- **Structural characterization of magnetic and highly correlated oxide nanomaterials**
  - **Inelastic neutron scattering**
  - **Wide-ranging experimental conditions**
- **Structural characterization of nanoporous materials**
  - **SANS**
  - **Inelastic neutron scattering**





CNMS provides unique capabilities

- ***High-yield* synthesis of magnetically 0D and 1D nanomaterials (quantum dots and wires)**
  - **CVD and catalyzed-CVD synthesis**
  - **High-temperature reverse micelles**
  - **Solvothermal synthesis**
  - **Templated growth**
- ***High-yield* synthesis of functional nanoporous materials (e.g., carbon and oxides)**
  - **Self-assembly methodologies**
  - **New templates for tailored materials**

These capabilities enable using neutron scattering to probe important mesoscale and nanoscale

Scientific Issues

Effects of quantum confinement and reduced dimensionality

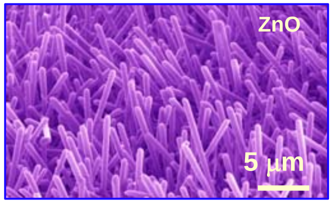
Behaviors of magnetic and electronic phases

Studies of adsorbed species in nano- tubes / pores / surfaces

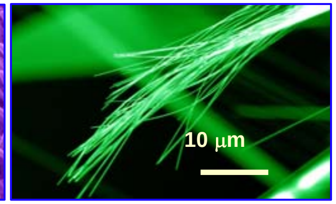
A CNMS Synergy of Co-Location

Functional Nanomaterials: High-Yield Nanomaterials Synthesis for Neutron Scattering

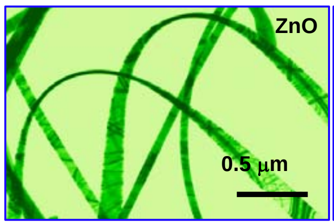
P.O.C. Zhengwei Pan panz@ornl.gov



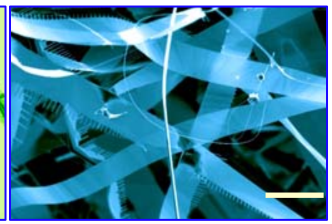
Nanorods

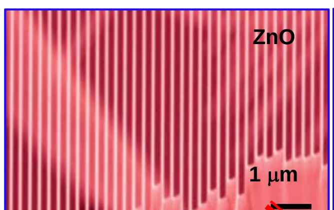


Nanowires

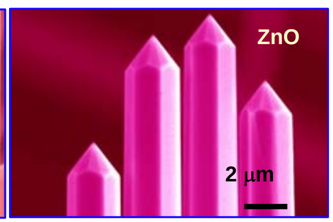


Nanobelts


Nanoribbons



Combs



Styluses

CNMS provides unique capabilities

- ***High-yield*** **synthesis of magnetically 0D and 1D nanomaterials (quantum dots and wires)**
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Scientific Issues

Effects of quantum confinement and reduced dimensionality

Behaviors of magnetic and electronic phases

Studies of adsorbed species in nano- tubes / pores / surfaces

The Outstanding Challenge of 21st Century Science that can be Addressed Using Neutron Scattering

The 21st Century Scientific Grand Challenge

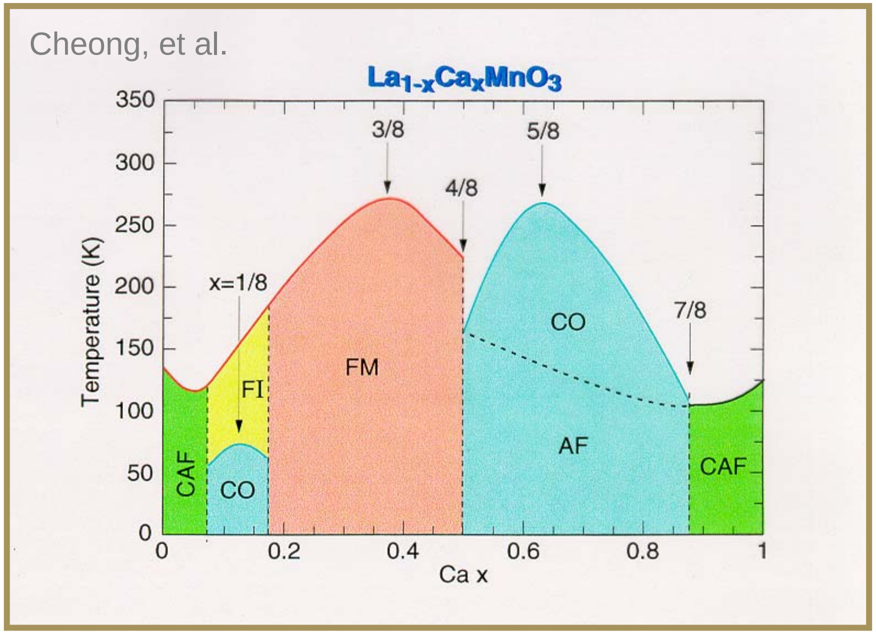
To understand self-organizing behavior that first emerges on the nanoscale in complex systems, and use it to create materials with greatly enhanced or new combinations of properties

"CORRELATED ELECTRON" MATERIALS

- **DISCOVERIES of many important properties not understood using traditional ideas**
  Copper-oxide high-temperature superconductors; metallic NiO; colossal magnetoresistance (CMR) in transition metal oxides; heavy-Fermion metals (rare earths and actinides); 1D and 2D electron gases; organic charge-transfer compounds

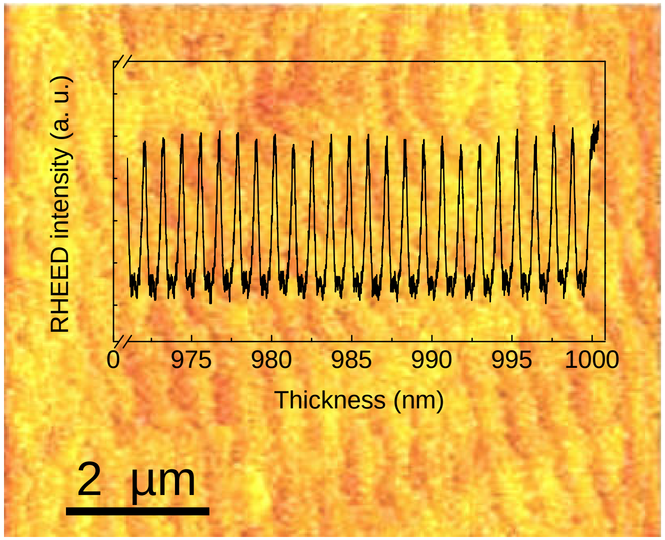
- **CHARACTERISTIC: COEXISTENCE of different kinds of collective ORDERING**
  -- Charge, orbital, spin density, super-conductivity, magnetism
  -- COMPETING or SYNERGISTIC ordering ?

- **ORIGIN: Breakdown of the independent-electron approximation**
  -- Strongly interacting electrons behavior is "highly correlated"
  -- Mathematical description being developed
  Field theory: ground & lowest excited states
  Numerical calculations: leadership computers + new, efficient algorithms
  -- *National leaders at ORNL + strong collaborators*



CNMS "Superlattice Crystals" for Forefront Neutron Science: A CNMS-SNS Synergy of Co-Location

RHEED oscillations used to monitor growth of unit cells #975 - 1,000



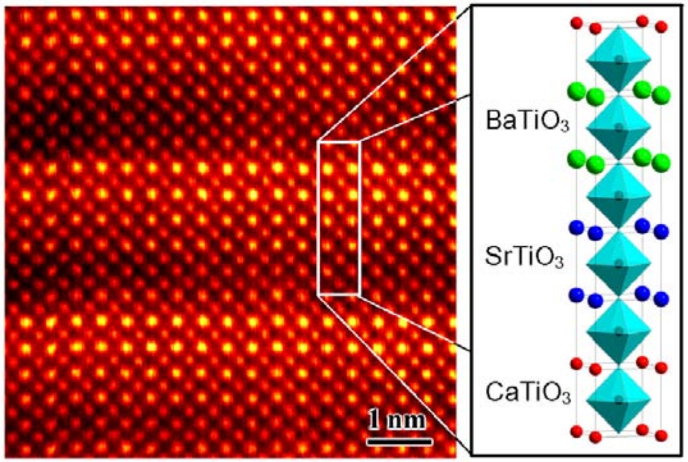
❑ NEW CAPABILITIES FOR OXIDES GROWTH

- New understanding and methods of ***pulsed laser deposition (PLD)*** from CMSD / ORNL.
- Enable growth of ***thick*** oxide heterostructures, suitable for ***all*** neutron scattering methods, ***with atomic-layer control.***
- ***Demonstrated:*** Growth of thousands of unit cells **with atomic-layer control**, **complete reproducibility,** and preservation of initial **surface quality (RHEED and AFM).**

❑ HIGH SCIENTIFIC IMPACT

- Used to carry out out ***first experimental verification*** of theoretically predicted polarization enhancements in ***artificial PLD ferroelectric*** *"superlattice crystals"*.
- Grown from repeated stacking of $SrTiO_3$, $BaTiO_3$, and $CaTiO_3$ building blocks with atomic-layer control.

[H.N. Lee et al., ***Nature*** 433, 395 (2005)]



Compositionally abrupt atomic interfaces as seen using Z-contrast STEM

But What is Needed and Why?
What are the Current Limitations for Neutron Scattering?

SINGLE-CRYSTAL SAMPLES FOR THE MOST REVEALING EXPERIMENTS

- ❑ Reflectometry, diffraction (structure), inelastic scattering (dynamics)
- ❑ Inelastic neutron scattering: Elementary excitations and dynamics
  -- Requires significant sample mass: 50-100 mg at SNS
- ❑ (Birgenau & Kastner) Japanese leadership in correlated electron materials research due to high value placed on single-crystal growers in Japanese universities

SERIOUS LIMITATIONS OF CONVENTIONAL "BULK" CRYSTAL GROWTH

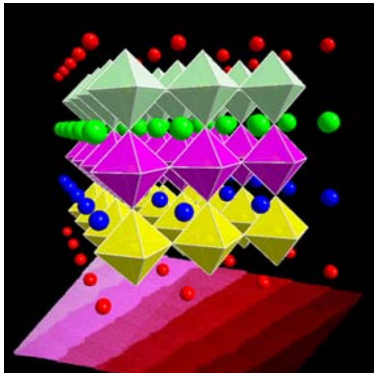
- ❑ Chemical composition, temperature, pressure are the only variables
- ❑ Limited to "naturally" occurring equilibrium phases → *unable* to enhance, "tune", or create the most interesting exotic properties
  -- Example: multiferroics, e.g., coexistence of ferromagnetism and ferroelectricity
  Few "natural" multiferroics and only weakly ferroelectric

Crystal growth methods needed that enable NANOSCALE MODIFICATION and CONTROL of self-organization and ordering

Growth of Artificially Layered Crystals Now is Feasible for the Full Range of Neutron Scattering Experiments

What heterostructure mass or thickness is needed for neutron scattering?

- ***Reflectometry:*** **0.5 μm – 5 μm thickness**
- ***Diffraction:*** **20 mg / 40 μm sufficient for complete structure determination in < 2 hrs at SNS**
- ***Inelastic:*** **~50 mg / ~100 μm necessary for detailed data analysis**



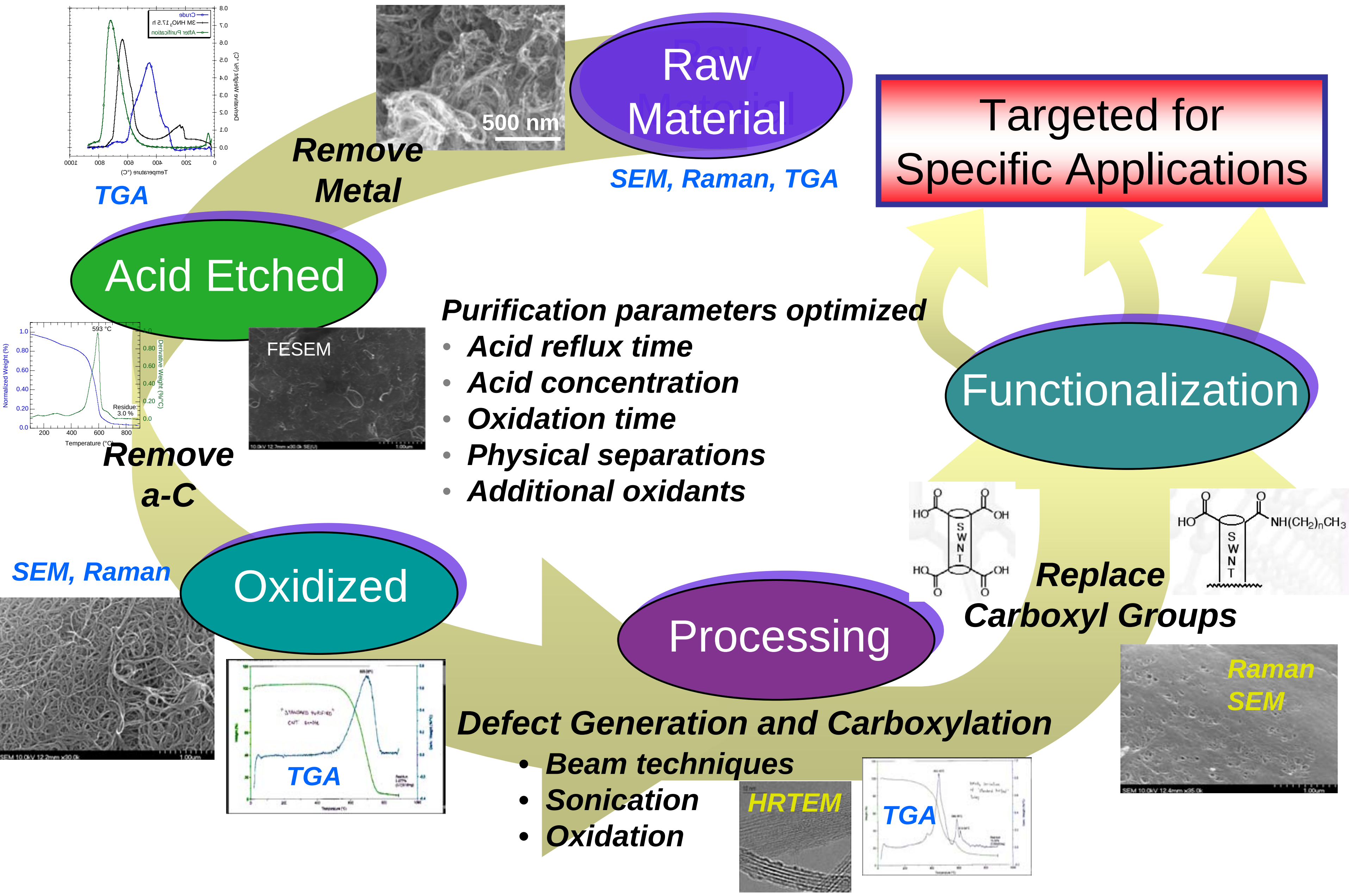
Nature, Vol. 433,
“News and Views” (2005)

OUTSTANDING <u>OPPORTUNITY</u> AND <u>NEED</u> TO BUILD A “SUPERLATTICE CRYSTAL” GROWTH FACILITY FOR NEUTRON SCATTERING

- **Move neutron scattering *beyond limits of conventional crystal growth***
- ***Science Driver:*** **Novel properties result from *competition* between nanostructure dimensions and characteristic length scales for collective phenomena**
  → capability for *nanoscale control* of individual layer dimensions *is essential*
- ***Rich opportunity!*** **Complex oxide family: Insulators, conductors, magnets, HTS**
  <u>Example</u>: *Combine* ferroelectric and ferromagnetic building blocks. What will be resulting properties? Strongly multiferroic designer crystals?
- ***CNMS and SNS:*** **Need to make the *DESIGN* of novel samples an integral part of the planning process for neutron scattering.**

Vision for Outstanding Synthesis Science

Unique Expertise: Synthesis & Processing of HP SWNTs



SANS: Surfactant to disperse bundled nanotubes in solution + micelle formation by surfactant molecules

NANO LETTERS
2004
Vol. 4, No. 9
1789−1793

Dispersing Single-Walled Carbon Nanotubes with Surfactants: A Small Angle Neutron Scattering Study

Howard Wang,*,† Wei Zhou,‡ Derek L. Ho,§ Karen I. Winey,‡ John E. Fischer,‡ Charles J. Glinka,§ and Erik K. Hobbie§

Department of Materials Science and Engineering, Michigan Technological University, Houghton, Michigan 49931, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received July 3, 2004

ABSTRACT

We have investigated the dispersion of single-walled carbon nanotubes (SWNTs) in heavy water with the surfactant octyl-phenol-ethoxylate (Triton X-100) using small angle neutron scattering. The results indicate an optimal surfactant concentration for dispersion, which we suggest results from competition between maximization of surfactant adsorption onto SWNT surfaces and a depletion interaction between SWNT bundles mediated by surfactant micelles. The latter effect drives SWNT reaggregation above a critical volume fraction of micelles. These behaviors could be general in dispersing SWNTs using amphiphilic surfactant. The data also reveal significant incoherent scattering from hydrogen in SWNTs, most likely due to acid and water residues from the purification process.

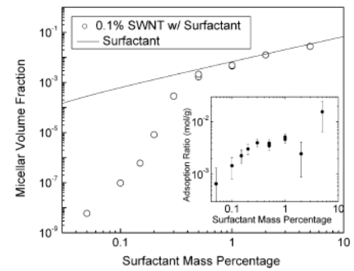


Figure 3. Micellar volume fraction in 0.1% SWNT suspensions (open circles) and surfactant solutions (solid curve) as a function of the overall surfactant concentration. Their comparison suggests that below 0.5% surfactant concentration, most surfactant molecules do not form micelles, whereas at high concentrations micellar formation dominates. The inset shows molar surfactant adsorption per gram of SWNT as a function of surfactant weight percentage in suspensions. Adsorption increases with surfactant concentration and saturates around 0.5% to 1%. The saturation adsorption ratio is ca. 0.004 moles/gram.

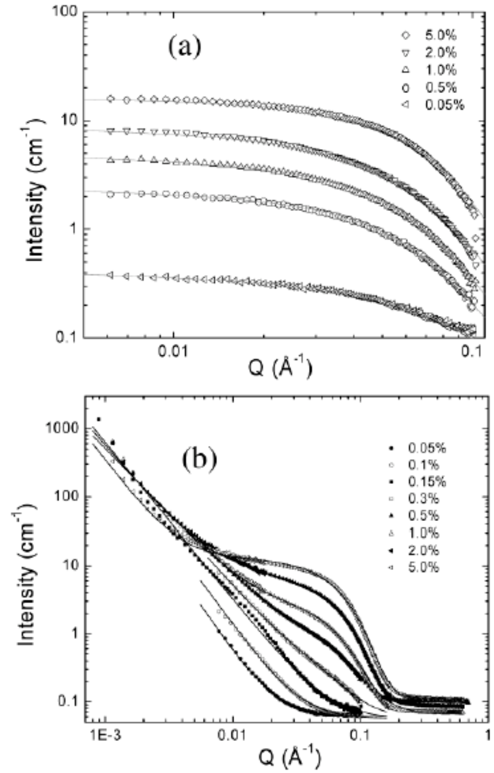


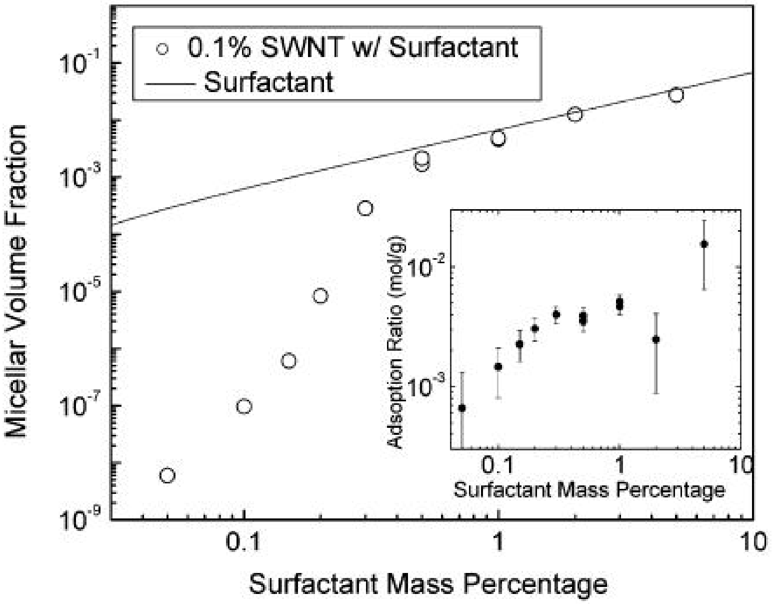
Figure 1. (a) SANS spectra of the Triton X-100 solution of various concentrations. The solid curves through the symbols are the best fits according to a micelle model as described in the text. The average radius of micelles is ca. 30 Å and the dispersity of radius $\Delta R/R_0 \approx 0.3$. (b) SANS spectra of SWNT/surfactant suspensions with 0.1% SWNT by mass and various surfactant concentrations ranging from 0.05% to 5%. The solid curves through symbols are the best model fitting.

Finds an optimum surfactant concentration for good dispersion of SWNTs, in presence of surfactant molecules and micelles

General picture provides guidance for optimal use of surfactants…

Dispersion and re-aggregation driven by different contributions to the system (SWNT + surfactant) free energy

Micellar volume fraction in 0.1% SWNT solutions (CIRCLES) and pure surfactant solutions (LINE), as a function of overall surfactant concentration.



INTERPRETATION

BELOW 0.5% CONCENTRATION -- Most surfactant molecules do not form micelles, but adsorb onto SWNTs.

HIGH CONCENTRATIONS – Micellar formation dominates.

Dynamic balance: Surfactant molecules can exist in three states

- ***Individual molecules in solution***
- ***In micelles (in solution)***
- ***Adsorbed onto SWNT surfaces***

Improvement of SWNT dispersion at low surfactant concentration

- ***Dynamic equilibrium between free surfactant in solution and adsorbed onto SWNTs***
- ***Increasing surfactant shifts balance toward larger SWNT surface for adsorption → better dispersion***

Deterioration of dispersion at high surfactant concentration

- ***Micellar formation increases rapidly above 0.1% surfactant concentration***
- ***Model micelles as hard spheres, mixed with rods (SWNTs) in solution***
- ***Re-aggregation of SWNTs in bundles →net free energy decrease from increase in free volume available to micelles***

Conclusions

NANO LETTERS
2004
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Howard Wang,[*,†] Wei Zhou,[‡] Derek L. Ho,[§] Karen I. Winey,[‡] John E. Fischer,[‡] Charles J. Glinka,[§] and Erik K. Hobbie[§]

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- **Finds a critical surfactant concentration for dispersion of SWNTs**
  Triton X-100 NOT ideal for SWNTs
- **General model for surfactant behavior provides guidance for optimal dispersion of SWNTs**

IMPACT AND OPPORTUNITY

- **Need to optimize surfactant(s) used for SWNT dispersion**
  Key capability for applications
  Neutron scattering can do this
- **Need for clean, pure SWNTs**
  Current strength of CNMS synthesis

Hydrogen Storage: Ti-decorated nanotubes

PRL **94,** 175501 (2005) PHYSICAL REVIEW LETTERS week ending 6 MAY 2005

Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium

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[1]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[2]*Physics Department, Bilkent University, 06800 Bilkent, Ankara, Turkey*
(Received 5 November 2004; published 5 May 2005)

We report a first-principles study, which demonstrates that a single Ti atom coated on a single-walled nanotube (SWNT) binds up to four hydrogen molecules. The first H_2 adsorption is dissociative with no energy barrier while the other three adsorptions are molecular with significantly elongated H-H bonds. At high Ti coverage we show that a SWNT can strongly adsorb up to 8 wt % hydrogen. These results advance our fundamental understanding of dissociative adsorption of hydrogen in nanostructures and suggest new routes to better storage and catalyst materials.

DOI: 10.1103/PhysRevLett.94.175501 PACS numbers: 81.07.De, 68.43.-h, 84.60.Ve

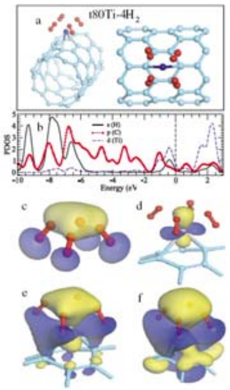


FIG. 2 (color). (a) Two different views of the optimized structure of t80Ti-4H_2. The relevant structural parameters are H-H = 0.84 Å, Ti-H = 1.9 Å, Ti-C = 2.17 Å, Ti-C′ = 2.4 Å. (b) The PDOS at the Γ point contributed from Ti, four H_2 molecules, and the six carbons of the hexagon on which Ti and H_2 molecules are bonded. (c) The σ^* antibonding orbital of four H_2 complex; (d)–(f) isosurface of the state just below E_F at three different values: at $\Psi = 0.08$, it is mainly Ti-d orbital; at $\Psi = 0.04$ the hybridization between the d orbital, two carbon π orbitals, and 4H_2 σ^* antibonding is apparent. At $\Psi = 0.02$ it is clear that the other four carbon atoms are also involved in the bonding.

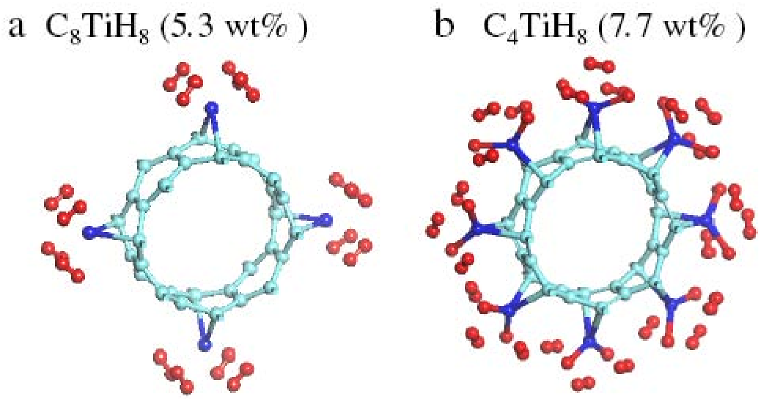


FIG. 3 (color online). Two high-density hydrogen coverage on a Ti-coated (8, 0) nanotube.

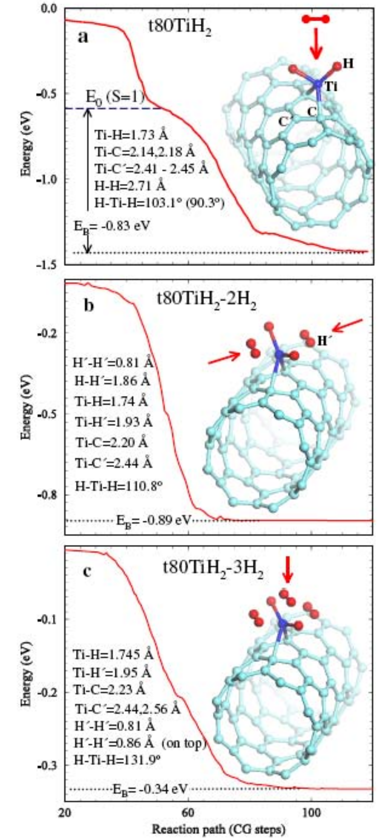


FIG. 1 (color online). Energy vs reaction paths for successive dissociative and molecular adsorption of H_2 over a single Ti-coated (8, 0) nanotube. (a) H_2 + t80Ti → t80TiH_2. (b) 2H_2 + t80TiH_2 → t80TiH_2 − 2H_2. (c) H_2 + t80TiH_2 − 2H_2 → t80TiH_2 − 3H_2. The zero of energy is taken as the sum of the energies of two reactants. The relevant bond distances and binding energies (E_B) are also given.

Can bond lengths, vibrational states, hydrogen uptake be measured by Neutron Scattering?

CNMS

Oak Ridge National Laboratory

Center for Nanophase Materials Sciences

www.cnms.ornl.gov

Importance of "Superlattice Crystals" for Forefront Neutron Science and User Research

❑ RESULT: A UNIQUE CRYSTAL-*DESIGN* CAPABILITY

- ***Novel properties*** result from competition between the dimensions of nanostructures and length scales relevant to collective phenomena
  → ***ability to control dimensions at the nanoscale is crucial*** for understanding
- ***Atomic-scale tailoring*** of artificial structures ***fundamentally different from those in Nature enables DESIGN*** of oxide "superlattice crystals" with specific new properties.
- ***Rich opportunity!*** Compatible oxides include insulators, conductors, ferro- and antiferromagnets, high-temperature superconductors, and CMR phases.
- ***What will be the properties*** of a superlattice made from ferroelectric ***and*** ferromagnetic building blocks? → **Future direction**: ***multiferroic***-oxide "designer crystals"
- "The ***DESIGN*** of novel samples should be ***an integral part of the planning process*** for neutron scattering." (Paul Canfield, Ames Laboratory, NHMFL Workshop)

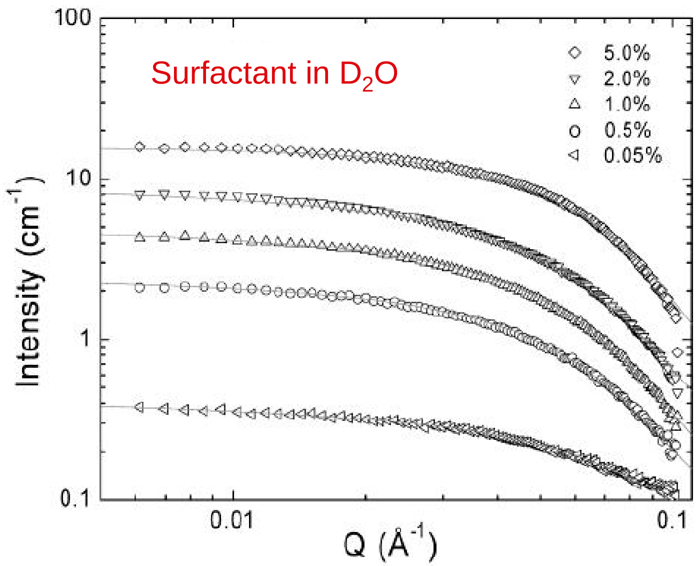
❑ IMPORTANCE of the CHALLENGE and of NEUTRON SCATTERING METHODS

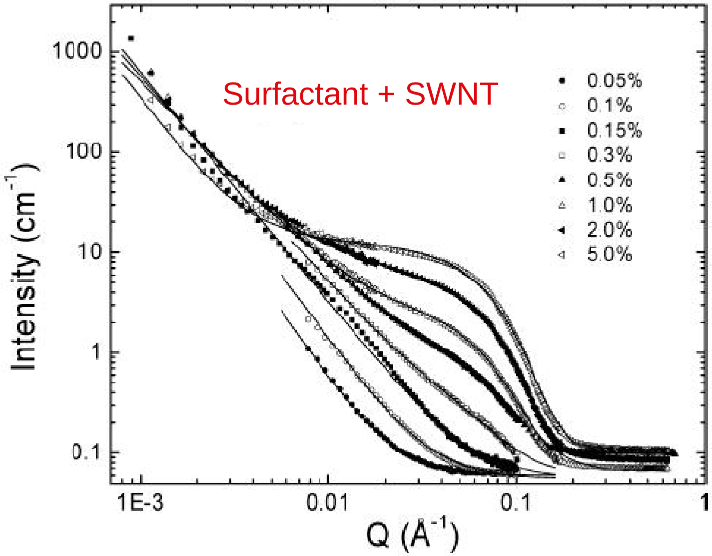
– "Clearly, ***highly correlated electron systems*** present us with ***profound new problems*** that almost certainly will represent ***deep and formidable challenges well into this new century…"***

– "…***neutron scattering is an absolutely indispensable tool*** for studying the exotic magnetic and charge ordering exhibited by highly correlated electronic systems."

R. J. Birgeneau and M. A. Kastner, Editorial, *Science* 288, 437 (21 April 2000)

SANS Spectra: Surfactant (only) in solution, or SWNTs + surfactant in solution





Single wall carbon nanotubes (SWNTs)

- ***HiPco process, followed by purification***
  - ***-- < 1% Fe + acid + water impurities***

Surfactant solutions in D_2O

- ***Triton X-100 surfactant, nonionic***
  - ***-- Known to disperse SWNTs***
  - ***-- "Clean" in SANS spectra: Dominant structure noninteracting micelles → single form factor, easily separated from SWNTs***
  - ***-- Concentrations 0.05% → 5%***
  - ***-- SANS data fit to spherical micelle model***
    R ~ 3.0 nm, ΔR/R ~ 0.30

Solutions with SWNTs

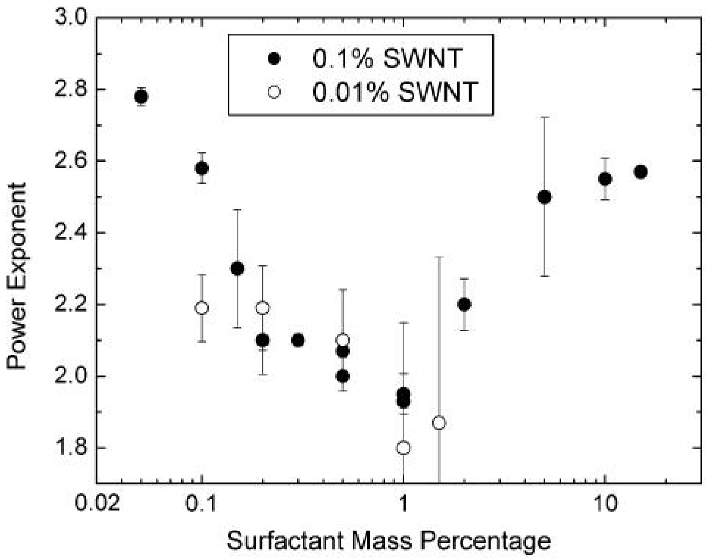
- ***SWNTs → power-law scattering at low-Q***
- ***Surfactant in solution + micelles at intermed-Q***
- ***Impurities → incoherent background scattering***
  Evident as "flat" background at high-Q

$$\frac{d\Sigma}{d\Omega}(Q) = \left.\frac{d\Sigma}{d\Omega}\right|_{SWNT} + \left.\frac{d\Sigma}{d\Omega}\right|_{Triton} + I_{inc} =$$

$$\frac{I_0}{Q^{\alpha}} + I_{Triton}(Q,\phi_{micelle}) + I_{inc}$$

SWNTs: Power-law scattering reveals optimum surfactant concentration for dispersion

Power-law exponent plotted vs. surfactant mass percent in solution, for 0.01% and 0.1% SWNT suspensions



Power-law exponent has clear minimum around 0.5% – 1% surfactant concentration

Model neutron scattering by SWNTs

- ***Rigid rods with L >> D***
  -- D ~ 1-2 nm   100 nm < L < few μm
- ***Scattered intensity ~ Q^{-1} for 1/L < Q < 1/D***

Previous neutron scattering from SWNTs

- ***Suspensions, polymer composites***
- ***Intensity ~ $Q^{-\alpha}$ with $2 < \alpha < 3$***
- ***$\alpha > 1$: Branching and wide distribution of sizes and structures***

Use α-values to assess degree of SWNT dispersion

- ***Values close to 1 → good dispersion***

Results of scattering measurements

- ***$\alpha > 1.8$ for both surfactant concentrations***
- ***Optimum surfactant concentration: 0.5% - 1%***
- ***Triton X-100 not ideal surfactant for SWNTs***

Why a minimum in the power-law exponent?