Recent Advances in Intelligent Bio-Nano Materials and Structures Research

Dimitris C. Lagoudas, Institute Director
Daniel C. Davis, Director of Operations

Texas Institute for Intelligent Bio-Nano Materials and Structures for Aerospace Vehicles

France – US Workshop on Nano Bio Technologies
March 2-3, 2006
Washington, DC

Bio-Inspired Design and Processing of Multi-Functional Nano-Composites (BIMat)
- Design and modeling of hierarchically structured materials capable of bio-sensing catalysis and self-healing
  - Princeton
  - UCSB
  - U of NC
  - Nat’l Inst. Aerospace

Institute for Nanoelectronics and Computing (INAC)
- Develop fundamental knowledge and enabling technologies in: ultradense memory, ultraperformance devices, integrated sensors, and adaptive systems
  - Princeton
  - Northwestern
  - UCSD
  - U of T
  - UCSD

Institute for Intelligent Bio-Nano Materials and Structures for Aerospace Vehicles (TiiMS)
- Basic and applied research in the integration of sensing, computing, actuation and communication in smart materials
  - Texas A&M
  - Rice
  - Texas Tech
  - Rice
  - U of Houston

Center for Cell Mimetic Space Exploration (CMISE)
- Bio-informatics for the development of new, scalable nano-technologies in sensors, actuators and energy sources
  - UCLA
  - CSU
  - A&M
  - UIUC
Mission of TiiMS

Advance emerging bio-nano science and technologies that will be implemented in adaptive, shape controllable, intelligent micro and macro structures for next generation aircraft and space systems.

Catalyze the academic community to significantly enhance the education of the next generation of aerospace professionals.

UNIVERSITY PARTICIPANTS

- University of Texas at Arlington
- Texas A&M University
- University of Houston
- Rice University
- Prairie View A&M University
- Texas Southern University
In Memorial

Professor Richard E. Smalley
Rice University

Chief Scientist
Co-Principal Investigator
TiiMS Institute

Research and Education Thrust Areas
**Research Challenge:** Bridging the Length Scales - from Nanomaterials to Aerospace Systems

<table>
<thead>
<tr>
<th>Functionalized Single Wall Carbon Nanotube</th>
<th>Single Wall Cross-linked Carbon Nanotubes</th>
<th>Functionalized Dispersed Carbon Nanotubes</th>
<th>Multifunctional Composite</th>
<th>Intelligent Aerospace Vehicle</th>
</tr>
</thead>
</table>

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**10^{-10}m**  
**10^{2}m**

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**Research Thrust:** Functionalized Nanomaterials

**Research Activities:**
- Nanotube purification, functionalization, separation and dispersion.
- Strength and toughness of organic and inorganic nanocomposites.
- Polymeric nanocomposites for multifunctional use with improved conductivity properties.
- Studying multifunctionality of nanocomposites

Nanostructures: 100 times stronger than steel at 1/6 the weight.
# Functionalized Nanomaterials

<table>
<thead>
<tr>
<th>Research Tasks for Group A Functionalized Nanomaterials</th>
<th>PI's Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production and functionalization of Carbon Nanotubes (CNT)</td>
<td>Tour, Barrera, Smalley</td>
</tr>
<tr>
<td>a. multifunctional CNT</td>
<td></td>
</tr>
<tr>
<td>b. electrically tunable CNT</td>
<td></td>
</tr>
<tr>
<td>c. self-healing of nanocomposites</td>
<td></td>
</tr>
<tr>
<td>d. other URETI uses</td>
<td></td>
</tr>
<tr>
<td>Synthesis and characterization of nanocomposites</td>
<td>Barrera, Krishnamoorti, Lee, Lagoudas, Wilkins, Ounaies</td>
</tr>
<tr>
<td>a. high strength carbon fiber</td>
<td></td>
</tr>
<tr>
<td>b. ceramic</td>
<td></td>
</tr>
<tr>
<td>c. elastomeric</td>
<td></td>
</tr>
<tr>
<td>d. structural and radiation protection</td>
<td></td>
</tr>
</tbody>
</table>

**Process for sidewall initiated polymerization**

Functionalized unroped separated nanotubes to enable structural enhancements

**Functionalized nanotubes dispersed in a polymer**

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**Functionalized Nanomaterials (Cont)**

<table>
<thead>
<tr>
<th>Research Tasks for Group A Functionalized Nanomaterials</th>
<th>PI's Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Development by integration &amp; hybrids and scale-up of materials fabrication (Beginning Year 4)</td>
<td>Barrera, Krishnamoorti</td>
</tr>
<tr>
<td>Critical testing and characterization for aerospace use of nanocomposites</td>
<td>Barrera, Lagoudas, Boyd, Krishnamoorti, Davis, Ounaies</td>
</tr>
<tr>
<td>Integration of nanocomposites into morphing wing &amp; multifunctional space structure. (Beginning Year 3)</td>
<td>Boyd, Lagoudas, Junkins, Valasek, Rediniotis, Halas, Barrera</td>
</tr>
</tbody>
</table>

**Rheological methods for dispersion quantification**

- Improved mechanical properties in SWCNT - reinforced elastomer

**Significant enhancements with NT concentrations**
Reinforced PPF polymer with Functionalized SWNTs

Single-Walled Carbon Nanotubes

Sidewall functionalization

Poly(ε-caprolactone) nanocomposites using Surfactants

Non-Covalent Polymer Wrapping

Non-Covalent Surfactant Adsorption

(R. Lee, R. Krishnamoorti @ UH)
Elastomeric Reinforcement (Siloxane) by Functionalized SWNTs

Tour

Composition dependence

T = 30 °C

Normalized Tensile Modulus

Elongation at Break

wt % SWNT

Technology licensed, being commercialized for annular blowout preventers (BOPs), elastomers enduring up to 20,000 psi with 90° ODs

J. Tour, Rice U.; R. Krishnamoorti, U. Houston; C. Dyke, NanoComposites Inc.,

TiiMS Research Leads to New Nanotechnology Companies

NASA URET research and Nanotubes from Richard Smalley that lead to commercial work and real revenue for two start-up companies.

NanoRidge Materials, Inc.
Houston, TX
CEO: Chris Lundberg
CTO: Enrique Barrera
Initial funding raised
Four initial projects for NASA, DOD, and a a polymer Co.
Licensed key IP
~50% Improvement in Z-axis properties for composites currently being sold.

NanoComposites, LLC
Houston, TX
CEO: Barry Drayson
CTO: Chris Dyke
CTAdvisor: James Tour
Initial funding raised
Key project with Hydril
Licensed key IP
Three times the strength increase in rubber. An Oil Field o-ring that was shown at the Offshore Technology Conference in Houston, TX.

VARTM used to make large components.

Microwave processing gives a new approach.
Research Thrust:
Multifunctional Material Systems

Research Activities:
- Multifunctional materials and systems at nano – micro – meso - macro physical length scales.
- Experimental validations of hierarchical material models for structural, electrical, and thermal functionality.
- Integrate porous SMAs into smart structures relevant to multifunctional lightweight space applications and shape control of morphing wings.
- Life assessment of multifunctional nanocomposite materials and structures.

Multifunctional Material Systems

<table>
<thead>
<tr>
<th>Research Tasks for Group B Multifunctional Materials Systems</th>
<th>PI’s Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Develop hierarchical material models for supercapacitors, porous SMAs, and other devices and materials</td>
<td>Boyd, Whitcomb, Chen, Lagoudas</td>
</tr>
<tr>
<td>Produce supercapacitors, porous shape memory alloys, and other devices and materials</td>
<td>Boyd, Ounaies, Chen</td>
</tr>
<tr>
<td>Experimentally validate hierarchical material models for stiffness, strength, fracture toughness, power, thermal conductivity, and shape memory effects (Began Year 2)</td>
<td>Davis, Chen, Ounaies, Boyd, Lagoudas, Hadjiev</td>
</tr>
</tbody>
</table>

Proposed Multifunctional Structural Supercapacitors Design using SWCNTs

NiTi sample showing electric current induced bonding between particles

Electro-magneto-elastic Composite Materials
Multifunctional Material Systems (Cont)

<table>
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<tr>
<th>Research Tasks for Group B Multifunctional Materials Systems</th>
<th>PI’s Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrate supercapacitors, porous shape memory alloys, and other devices and materials into multifunctional structural components (Beginning Year 4)</td>
<td>Boyd, Lagoudas, Chen, Ounaies</td>
</tr>
<tr>
<td>Produce hybrid solid state materials for integrated intelligent systems</td>
<td>Kirk</td>
</tr>
<tr>
<td>Develop nanocomposites applicable for stress sensing and other multifunctional capabilities using nanotubes, other nano-inclusions and nanoshells (Beginning Year 4)</td>
<td>Barrera, Ounaies, Halas</td>
</tr>
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</table>

**Eutectic Alloy Nanowires**

**Optics at the nanoscale!**

Nanoshells for nanophotonics:
Stress sensing, biomedical, new sensors

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**Actuation Characteristics of Multifunctional Materials**

- **Electroactive Ceramics**
- **Ionic / Electronic Conducting Polymers**
- **Dielectric Elastomer**
- **Carbon Nanotubes**
- **Magnetic Shape Memory Alloys (MSMA)**
- **Shape Memory Alloys (SMAs)**

**I-PVDF**

Based on Original Graph by Don Leo, VPI
Active Nanocomposite Materials for Multifunctional Applications

**Fabrication**
- Capabilities for synthesis and fabrication of:
  - Thin film
  - Non-woven mats
  - Nanofiber
  - Bulk films

**Characterization and Testing**
- Extensive Characterization Capabilities in:
  - Electromechanical coupling characterization
  - Nanoparticle-polymer interaction by spectroscopy, FTIR, HRSEM, AFM, and XRD
  - Static and dynamic mechanical characterization
  - Thermal characterization

**Multifunctional Materials:**
- Electric field-driven anisotropic dispersion of nanoparticles in thin films
- Change of property with designed-in anisotropy
- Polymer in liquid form
- Nanoparticles: Carbon nanotubes, exfoliated graphite oxide, graphite, ceramic particles

**Modeling and Simulation**
- Effective media approach
- Thermodynamically-based constitutive modeling for multifunctional materials

Polymer Nanocomposites as Sensors and Actuators

**Random Composites:** Bending Electrostriction

**Aligned and Patterned Composites**

**Enhanced Piezoelectricity**
- For 0% and 0.1% SWNT in 30-CBN/94 at 18 Hz
- For 0.1 wt% SWNT
- No SWNT

- Bending as a unimorph
Fabrication and Characterization metallic (Bi, Sn, Pb-Bi) nanowires

Hydraulic Injection method — cost effective method suitable for low melting metals and alloys with stochiometric composition

Well ordered pores from low purity Al

60nm diameter, 10μm long

Single crystal Nanowires: for interconnects, & sensors

Hydraulic Injection

Characterization

- mechanical - electrical

Challenges

Manipulation for integration with nano- and micro-devices

Quantum Dots

Size-dependent — Coupled Physical and Mechanical Behavior

Coupling to Opto-electronic Properties of Quantum Dots

Stresses and strains in nano-inclusions

Defects and impact on optoelectronic and mechanical properties

Nanocomposite and Multifunctional Thin Films

Pradeep Sharma @ UH
Research Thrust: Biomaterials and Devices

Research Activities:
- Integrate nanomaterials and biomaterials into multifunctional devices.
- Produce novel biomaterials (protein composites) with sealants and adhesives for structural self-healing.
- Develop Continuous Mixer for high shear mixing of SWNT and Bio-fluids.
- Investigate the toxicology of SWNT and nanocomposites.

Bio-Chemical Agent Sensors

Biomaterial and Devices

<table>
<thead>
<tr>
<th>Research Tasks for Group C Biomaterials and Devices</th>
<th>PI's Involved</th>
<th>Biopolymers as Dispersing Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterize and produce (natural elastomeric abductin) proteins</td>
<td>Ficht, Andrews</td>
<td></td>
</tr>
<tr>
<td>a. Produce chimeric genes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Produce catecholic proteins</td>
<td></td>
<td>Biopolymers as Dispersing Agent</td>
</tr>
<tr>
<td>Develop multifunctional devices that use catecholic proteins and abductin as sealants, adhesives, and structures (Beginning Year 4)</td>
<td>Andrews, Ficht</td>
<td></td>
</tr>
<tr>
<td>Develop stochastic sensing with membrane proteins, functionalized carbon nanotubes (Began in Year 2)</td>
<td>Bayley</td>
<td></td>
</tr>
<tr>
<td>Toxicology and human health</td>
<td>Clement, Ramesh, Jejelowo</td>
<td></td>
</tr>
<tr>
<td>Develop bio-chemical sensors</td>
<td>Jejelowo, Crooks</td>
<td></td>
</tr>
</tbody>
</table>

Development of a hand-held biosensor for analysis of DNA and proteins

Micro-encapsulation of self-healing materials

Design and Construction of a Stochastic Sensing Element Based on the α-hemolysin Protein Pore
A novel α-hemolysin mutant pore, αHL-(M113FK147N)₇, has been designed that is stable and functional at temperatures up to 100°C. The single-molecule nanopore chiral sensor at elevated temperatures might have important applications in exobiology and spacecraft.

Xiaofeng Kang, Stephen Cheley and Hagan Bayley @TAMU

Research Thrust: Multiscale Modeling

Research Activities:

- Theoretical and computational modeling of nanotube-polymeric molecular architectures and nanocomposites.
- Computational tools and methods to bridge the various length scales.
### Multiscale Modeling

<table>
<thead>
<tr>
<th>Multiscale Modeling Research Thrust</th>
<th>Objectives/Deliverables</th>
<th>PI's Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Develop hierarchical modeling tools from nano to macro scales that will allow multifunctionality to be designed into various length scales</td>
<td></td>
<td>Pettitt, Whitcomb, Wheeler, Yakobson, Sharma</td>
</tr>
<tr>
<td>Biominetics - Develop quantitative hierarchical models of the mechanical properties of cytoskeleton, with special attention to mimicking tensegrity.</td>
<td></td>
<td>Yakobson</td>
</tr>
<tr>
<td>Materials and Property Simulation</td>
<td></td>
<td>Yakobson, Pettitt, Whitcomb, Wheeler, Sharma</td>
</tr>
</tbody>
</table>

#### SWCNT Composite Idealization and Associated Length Scales

- **Graded Interphase Microscale**
- **CNT Bundle Scale**
- **CNT Scale**

- Randomly Oriented Bundles
- In-Plane Clustering in Bundles
- Interphase Regions

- Defects in carbon nanotubes
- Si$_{12}$Me$_n$nanowires
- Stable c3t Stable, Collapsing c3t8
- DNA strand diffusing in salty water on an organically functionalized surface
Characterization and Modeling of SWCNT Toughened CarbonFiber Composites

Interphase Region with Graded Material Properties (due to varying CNT volume fraction)

Composite Laminate Scale

Macroscopic Composite

Lamina Microscale

Fiber-Graded Interphase Scale

Characterization and Modeling of Nanocomposites

Multiscale Modeling

Atomistics

Amnaya Awasthi (TAMU)
Sarah Frankland (NIA)
Tom Clancy (NIA)

Micromechanics

Gary Seidel (TAMU)
Sarah Frankland (NIA)
Dan Hammerand (SNL)

Macromechanics

John Whitcomb (TAMU)
Jaret Riddick (NIA)

Fabrication and Characterization

Functionalization

Jiang Zhu (RICE)

Fabrication

Jiang Zhu (RICE)
Piyush Thakre (TAMU)

Characterization

Piyush Thakre (TAMU)
Helen Herring (NASA)
Victor Hadjiev (UH)

Co-ordinators:
Dr. T. Gates (NASA)
Dr. E. Barrera (RICE)
Dr. D. Lagoudas (TAMU)

Collaborators: Dr. D. Davis (TAMU), Dr. Z. Ounaies (TAMU)
Research Thrust: Intelligent Systems

Research Activities

- Develop sophisticated integrated engineered materials, sensing, and actuation systems with high strength-to-weight ratios.
- Develop autonomous control system designs with the robustness, intelligence and adaptability to accommodate distributed and hierarchical (multiscale) sensing and actuation.

Intelligent Systems

<table>
<thead>
<tr>
<th>Research Tasks for Group D Intelligent Systems</th>
<th>PI's Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro-modeling and validation (Began in Year 2)</td>
<td>Rediniotis, Valasek, Lin, Junkins, Nagarajaiah</td>
</tr>
<tr>
<td>Structured Adaptive Control</td>
<td>Valasek, Zimmerman, Nagarajaiah, Lin, Grigoriadis</td>
</tr>
<tr>
<td>Artificial Neural Networks</td>
<td>Junkins, Meade, Zimmerman, Nagarajaiah</td>
</tr>
<tr>
<td>Rules-Based Decision Theory &amp; Fault Detection (Began in Year 3)</td>
<td>Junkins, Meade, Valasek, Zimmerman, Nagarajaiah</td>
</tr>
<tr>
<td>Hierarchical functional coding algorithms (Beginning in Year 4)</td>
<td>Rediniotis, Valasek, Zimmerman, Junkins</td>
</tr>
</tbody>
</table>
Intelligent Systems (Cont)

<table>
<thead>
<tr>
<th>Research Tasks for Group D</th>
<th>PI’s Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adaptive shape control of reconfigurable structures (Began in Year 3)</td>
<td>Junkins, Rediniotis, Valasek</td>
</tr>
<tr>
<td>Adaptive mission planner (Began in Year 3)</td>
<td>Junkins, Valasek, Zimmerman</td>
</tr>
<tr>
<td>Drag and separation control (Began in Year 2)</td>
<td>Rediniotis, Junkins, Lin</td>
</tr>
<tr>
<td>Reconfigurable Smart Wing Experiment (Began in Year 2)</td>
<td>Rediniotis, Lin, Junkins</td>
</tr>
<tr>
<td>Integration of nanocomposites into morphing wing &amp; multifunctional space structure (Beginning in Year 4)</td>
<td></td>
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</table>

Morphing wing with CNT elastomer

Artificial Intelligence for Characterization of Shape Memory Alloy Materials

Learning the Hysteresis Behavior and Position Voltage Relationship Numerically

Graphs show that over the course of experience, Reinforcement Learning can determine how to get to a specific position via applied voltage, and the hysteresis behavior.

John Valasek @ TAMU
Biologically Inspired Systems: Enabling Aircraft and Spacecraft to Morph

Control Theory for Autonomous, Intelligent, Robust, and Adaptive Systems Comparable to Flying Birds

Original Research that Combines Traditional Control and Intelligent Control:

- Structured Adaptive Model Inversion Control (SAMI)
  - Flight controller to handle wide variation in dynamic properties due to shape change
- Machine Learning
  - Learns the optimal shape at every flight condition in real-time

Progress in Morphing Control and Simulation

U.S. Patent 2003: 2-D Plate
U.S. Patent 2004: Rectangular Block
U.S. Patent 2005: Ellipsoid
U.S. Patent 2006: Delta Wing

Final Objective

Morphing: Continuous Optimal Shape Control

John Valasek @ TAMU

TiiMS has developed strong collaborations with NASA Centers

Examples of collaborations:

- LaRC: Computational Methods / Modeling /Characterization /Nanomaterials
- LaRC: Multifunctional Material Systems
- LaRC: Integrated Tailored Aerospace Structures (ITAS)
- LaRC: Sensors and Biomaterials
- LaRC/JSC: Vehicle Health Monitoring
- LaRC/JSC: Platform Nanomaterials / Composites / Components
- Ames: Biomaterials /Thermal Protection Systems / Multiscale Modeling

NASA Relevance
Education and Outreach

Major Objectives:
• Train the next generation of aerospace engineers and scientists.
• Increase the number of engineers and scientists from under-represented groups.
• Introduce nano-science and engineering to K-12 schools through established and emerging education programs.
• Provide professional development opportunities for K-12 educators focusing on nanoscience and engineering initiatives.
• Provide training to students and educators in interdisciplinary education in science, mathematics, and engineering.

Undergraduates in Research –2005

Ross McLendon investigating dragon fly wing structure
Brian Hrycushko miniaturizing micro-SQUIDs
Brent Volk characterizing high temperature SMAs
Natalie Cygan fabricating protein nanocomposites

"The majority of the Institute’s budget will be spent on education."

Undergraduate Student Design
Undergraduates in Research –2005

Justin Maddox characterizing PVDF for bio applications
Marquita Bradshaw characterizing dendrimer encapsulated Co
Toren Watson finding the flexural properties of Epon 862

Field Trips

• NASA Johnson Space Center (JSC) in Houston, Texas
• The Zyvex Corporation in Richardson, Texas
• The University of Texas at Dallas in Richardson, Texas
• The Lockheed-Martin Corporation in Fort Worth, Texas

REU students in front of an F-16 at Lockheed Martin
Nanotechnology Presentation
In front of mock shuttle
Poster presentations can be seen at: tiims.tamu.edu/2005summerREU/presentations.html

REU Student Research Poster Prize Winners!!

Marquita Bradshaw won 1st place in Biomaterials and Devices and 1st place Overall

Jessica Fichuk won 1st place in Intelligent Systems

Holly Feldman won 3rd place in Intelligent Systems
Summary

• TiIMs consists of six thrust areas with strong interfaces.
• There is strong collaboration in research and education amongst the 6 institutions and 32 co-PIs
• TiIMs has developed collaborations with NASA Centers, national laboratories and industry.
• TiIMs is supporting and educating a significant number of students (pre-college, undergraduate, graduate) and post docs.
• The co-PIs are integrating bio-nanotechnologies into their courses and implementing curricular changes.
• Significant research advances have been achieved in the areas:
  – Functionalized nanomaterials
  – Multifunctional materials
  – Biomaterials and devices
  – Multiscale modeling
  – Intelligent systems
Thank You

http://TiiMS.TAMU.EDU