Scalable Manufacturing of Nano-composites using Controlled Assembly of Magnetic Nano-pillars

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Acknowledgment

• Technical assistance
  - Prof. Ellen Platzman (USC): magnetic measurement
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  - Dr. Risaku Toda: microfabrication
  - Dr. Rakesh Murthy: technical discussions
  - Dr. Daniel Wilson: AFM
  - Dr. Matthew Dickie: SEM

• Funding: Keck Institute for Space Studies, Ms. Michele Judd
• **Introduction** to the field
  - **Nano-/micro-engineered materials** for aero/astro applications
  - **Current challenges**: scalability
  - **Key steps** towards effective property scaling and scalable manufacturing

• **My study at JPL** to provide a solution to scalable manufacturing: magnetic assembly of nano-pillars

• **Research efforts to be continued**
Introduction
Nano-/Micro-Engineered Materials

Highly-organized and tailored structures to deliver unconventional properties and high performance
Highly-organized and tailored structures
to deliver unconventional properties and high performance
Merits of Going Small

- Advanced properties
  - Tailoring and optimization with structure design
  - High performance from high crystallinity
  - Unique properties due to size
  - Multi-functionality
- Light weight
Engineered Materials for Aero/Astro Applications

- Thermal insulation
- Anti/de-icing
- High temp. tolerance
- Light-weight
- SHM/NDE
- Vibration isolation
- Shieling against radiation, EMI, and debris
- Thermal protection
- Thermal management
- In-space operation
- Launch
  - Extreme environment
  - Light-weight
- Re-entry

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[All images, NASA]
Challenges of Engineered Materials

Nano-/micro-particles
[$\sim 10^{-9}-10^{-6} m$]

Aero/astro structures
[meters]

- Missing scalable manufacturing
- Poor property scaling

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[Lee et al., J. Am. Chem. Soc., 2002]

[Peng, Adv. Mat., 2003]

[NASA]
Challenge: Manufacturing

Nano-particle assembly

Highly-controlled

Poor

Micro-structure

Scaling

Mixing of nano-particles

Into matrices

Poor

Good

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[Thostenson et al., Carbon, 2006]

[Garcia et al., Comp. Sci. Tech., 2008]

[Velve, Science, 2000]

[Zeng, Nature Letter, 2002]
Challenge: Property Scaling

The example case with CNT-composites

Specific electrical conductivity $[(S/m)/(kg/m^3)]$

Specific thermal conductivity $[(W/mK)/(kg/m^3)]$

Metals
- Aluminum
- Steel
- Copper

Ceramics
- Alumina
- Carbon fiber (axial)

Foams
- SWNT individual
- MWNT bundles
- SWNT in polymer
- MWNT in polymer

Composites
- CFRP in-plane
- CFRP through-thickness
- GFRP
- Polymeric foams
- SWNT bundles
- MWNT bundles
- SWNT in polymeric
- MWNT in polymeric

SWNT individual

MWNT individual

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Key Technology Steps

… to apply \textit{bulk} engineered materials with \textit{fine nano-/micro-organization} for large-scale (aerospace) structures

- Scalable manufacturing methods
- Knowledge to optimize scaling
- Tools to enable multi-scale engineering
My Study at JPL:
Magnetic Assembly of Nano-Pillars
Overview: Magnetic Assembly of Nano-Pillars

Component
- Meso-scale
- Intrinsic anisotropy

Micro-Structuring
Control by external fields

Compositing
- Bulk processing
- Scalability

Manufacturing Flow

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Technical Approach

- **Fabricate magnetic nano-pillars**
  - Conformal coating of CNTs with ferromagnetic metals
  - Material characterization
  - Magnetic property characterization
- Achieve controlled magnetic assembly of nano-pillars
- Deliver high-performance, multi-functional composites with organized nano-pillar structures
Fabrication of Magnetic Nano-Pillars

- Previously: metal deposition on porous templates
  - Aspect ratio: ~100
- Novel fabrication: *conformal coating of CNTs with ferromagnetic metals*
  - High aspect ratio (~1000)
  - Bulk fabrication

Fabrication of Magnetic Nano-Pillars (continued)

1. Patterning of catalyst
   Photolithography using image reversal photoresist
   Mask
   PR
   Si
   E-beam metal dep:
   Al₂O₃ 30nm, and Fe 30 nm
   Lift-off

2. Chemical vapor deposition of aligned CNTs
   Ethylene/Ar introduction at 750°C
   100 µm
   10 µm
   1 µm
3. Controlled laying of CNTs

Directional collapse by capillary forces

4. E-beam deposition of metals

- Fe, Ni, and Co
- Thickness: ~50nm
Inspection of Fabricated Nano-Pillars: Metal Coating

- SEM: visual inspection of conformal coating
- AFM: metal-coated CNTs ~30-85nm vs. as-grown CNTs ~20-55nm

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Magnetization of Ferromagnetic Materials

Hysteresis loop

- $M$: measured magnetization
- $M_s$: saturation
- $M_r$: remanence
- $H_c$: coercivity
- $H$: applied magnetic field

Magnetic Characterization: Alternating Gradient Magnetometer

- Application of an alternating magnetic field
- Detection of oscillation (magnetic moment) by a piezoelectric vibration sensor
- High sensitivity ($10^{-8}$ emu), good for thin-film samples

• Magnetic nano-pillar samples
  • Aligned, metal-coated CNTs horizontally laid on a Si substrate
  • Consistent sample size and CNT density
• Baseline sample: deposition of metal layers, without CNTs

Magnetic Characterization: Nano-Pillar Samples

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**Measured Magnetic Properties: Fe Baseline**

- Ferromagnetic
- Small hysteresis
- Coercivity: comparable and slightly higher, due to impurities or stresses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hc [Oe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement</td>
<td>Fe 50nm on Si</td>
</tr>
<tr>
<td>Literature</td>
<td>Iron, high purity</td>
</tr>
<tr>
<td></td>
<td>Armco iron</td>
</tr>
<tr>
<td></td>
<td>Cast iron (annealed)</td>
</tr>
</tbody>
</table>

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[Kaye & Laby, Table of Physical & Chemical Constants]
Measured Magnetic Properties: Fe-Coated CNTs

- Ferromagnetic
- Different from Fe baseline
  - Magnetic moment without $H$
  - Hysteresis
  - Higher coercivity and remanence
  - Lower saturation
  - 2 phases
Magnetization of Ferromagnetic Materials

Magnetic domain structure

- Polycrystallites (grains), each with a certain magnetization direction
- Local magnetization depends on
  - Grain structure, size
  - Presence of impurities
  - Local stress
  - Balance of local energy
- Formation of magnetic domains through minimization of free energy

Measured Magnetic Properties: Fe-Coated CNTs (continued)

- Ferromagnetic
- Different from Fe baseline
  - Magnetic moment without $H$
  - Hysteresis
  - Higher coercivity and remanence
  - Lower saturation
  - 2 phases

More grains/domains
More defects
Anisotropic micro-structure?

Fe baseline
Conformally-coated Fe
2 phases observed at the 0° angle
- Mismatch between crystalline and CNT orientations
- CNT misalignments

6-nm-thick Fe film grown on Si (111) [Cougo dos Santos et al., Phys. Rev. B, 2000]
Measured Magnetic Properties: Fe-Coated CNTs (continued)

Measurement with the samples oriented against $H$ at an angle
- 2 phases observed regardless of the directions
- Slight shifting of coercivity, saturation, and remanence

![Graph showing magnetic properties at different angles](image)
**Measured Magnetic Properties: Fe-Coated CNTs (continued)**

*Dominant effect of micro-structure anisotropy*

- Both reduced remanent magnetization and coercivity decrease with the sample angle

[Cougo Dos Santos et al., Phys. Rev. B, 2000]
Co-coated CNTs: trends comparable with Fe, more defined 2phase

Ni-coated CNTs
- Minimal hysteresis
- Coercivity and remanence comparable with baseline
Fabrication of magnetic nano-pillars

- Established a simple fabrication method
  - High aspect ratio using CNT templates.
  - Conformal coating and scalability to be improved
- Evaluating the effects on magnetic properties from
  - Grains/domains: hysteresis
  - Micro-structuring: anisotropy
  - Metal-CNT binding/interfaces
Research Efforts to be Continued
Research Plan: Magnetic Assembly of Nano-Pillars

- Improve nano-pillar fabrication
  - Scalability
  - Capability to tailor magnetic properties
- Achieve controlled magnetic assembly of nano-pillars
  - In-situ observation
  - Assembly design through simulation
- Deliver high-performance, multi-functional composites with organized nano-pillar structures
  - In-situ pillar alignment
  - Micro-structure design for multi-functionality

[Ang, Carbon 1999] [Chen, Comp Sci Tech 2000] [Kong, Surface and Coatings Technology 2002]
Research Plan: Magnetic Assembly of Nano-Pillars (continued)

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Future Research Plan: Scalable Manufacturing

Experimental parametric studies in the lab scale
- Tailored mat. property
- Controlled assembly

Simulation studies

Knowledge and tools for multi-scale design

Application as functional nano-particle
[Prof. Mallouk, PSU]

Design and supply of bulk nano/micro-engineered materials
- Functional coating
[NASA]
- Bulk structures