

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

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# Acknowledgment

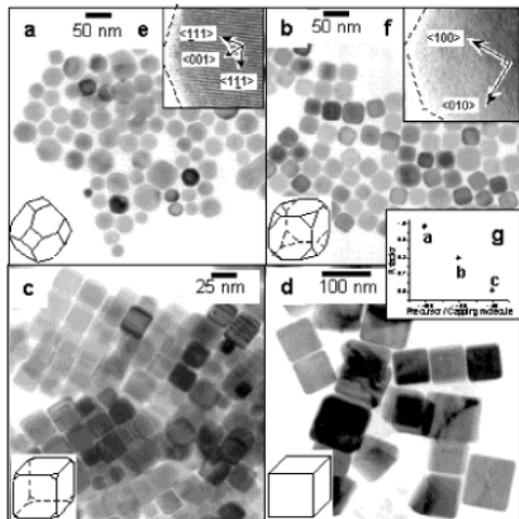
- Technical assistance
  - Prof. Ellen Platzman (**USC**): magnetic measurement
  - Dr. Valerie Scott: CNT synthesis
  - Dr. Risaku Toda: microfabrication
  - Dr. Rakesh Murthy: technical discussions
  - Dr. Daniel Wilson: AFM
  - Dr. Matthew Dickie: SEM
- Funding: Keck Institute for Space Studies, Ms. Michele Judd

# Outline

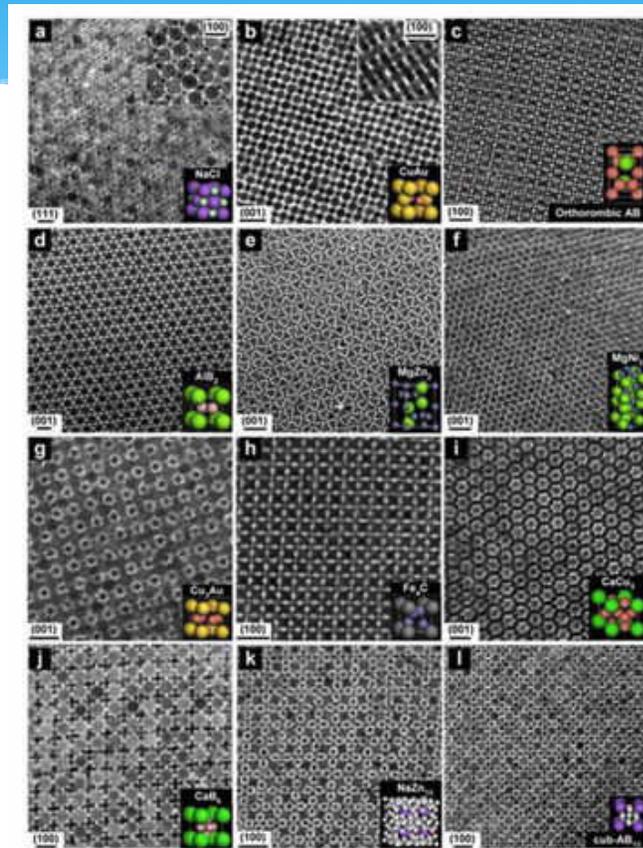
- **Introduction** to the field
  - **Nano-/micro-engineered materials** for aero/astro applications
  - **Current challenges**: scalability
  - **Key steps** towards effective property scaling and scalable manufacturing
- **My study at JPL** to provide a solution to scalable manufacturing: magnetic assembly of nano-pillars
- **Research efforts to be continued**

# Introduction

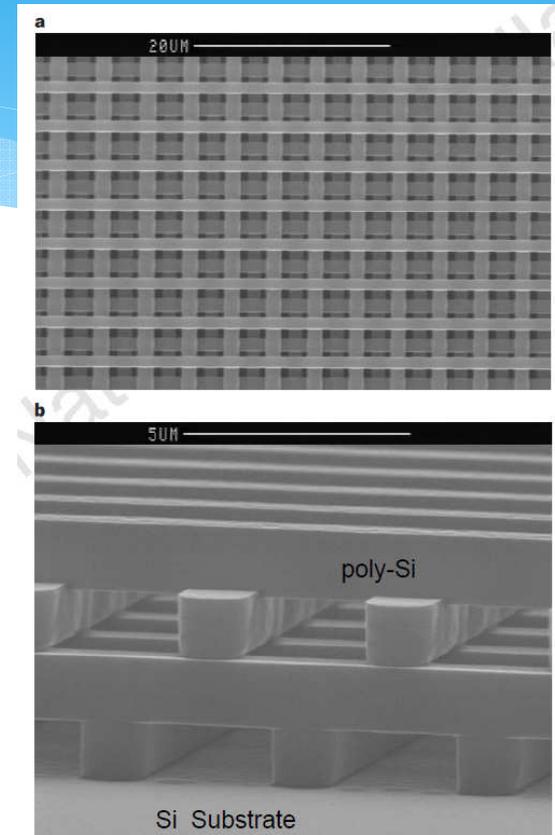
# Nano-/Micro-Engineered Materials



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



[Shevchenko et al., Nature, 2006]



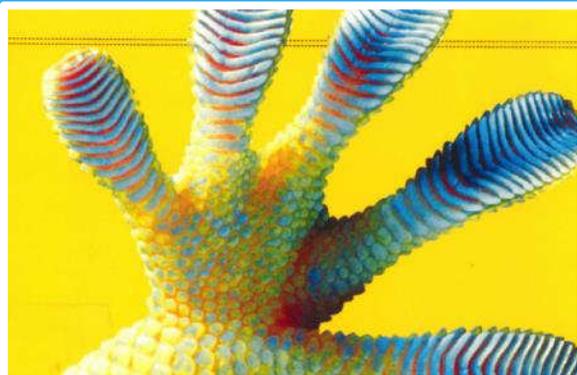
[Lin et al., Nature, 1998] *Micro*

**Nano**



**Highly-organized and tailored structures  
to deliver unconventional properties and high performance**

# Nano-/Micro-Engineered Materials

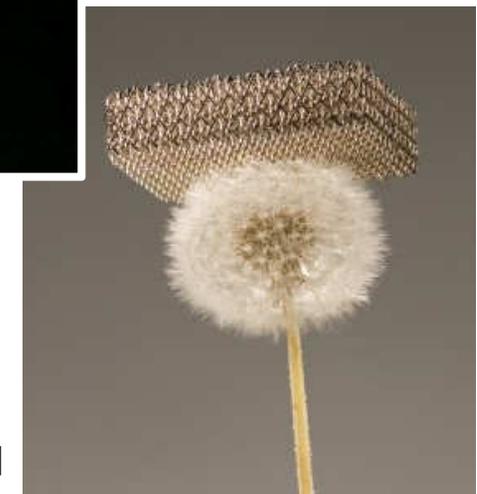
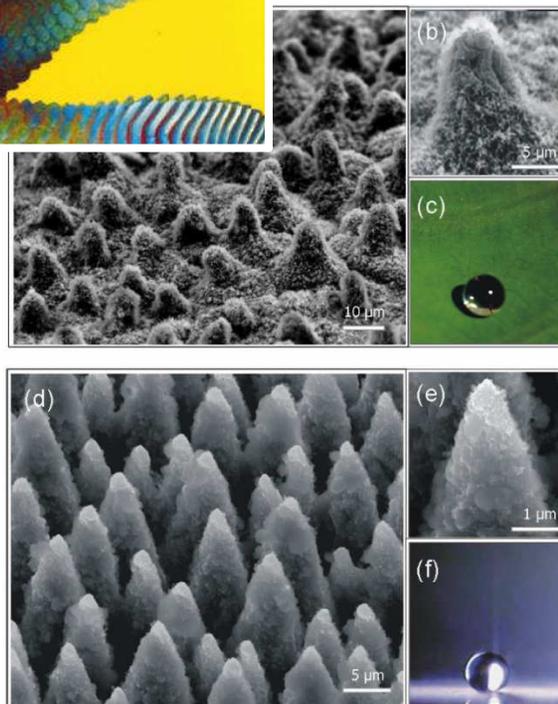


[Forbes, 2005]



[Lawrence Berkeley National Lab]

[Barberoglou, SPIE, 2009]



[HRL Lab, LLC]

Nano

Micro

**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

[All images, NASA]

Thermal insulation  
Anti/de-icing

Light-weight

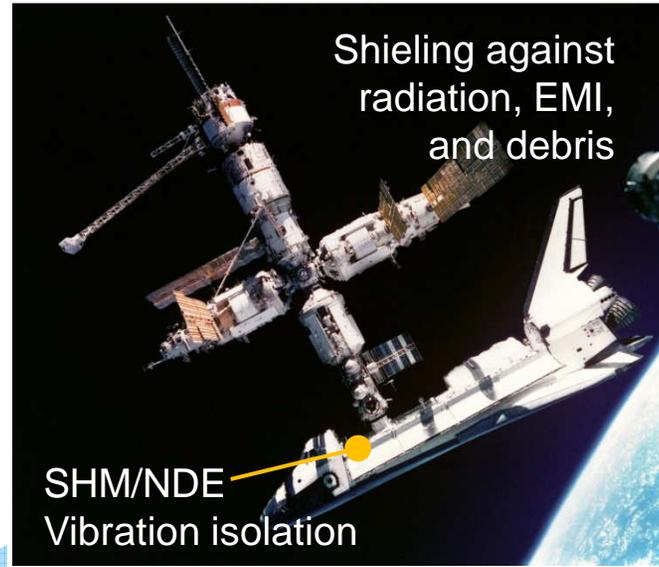
High temp. tolerance



*Launch*

Shielding against radiation, EMI, and debris

SHM/NDE  
Vibration isolation



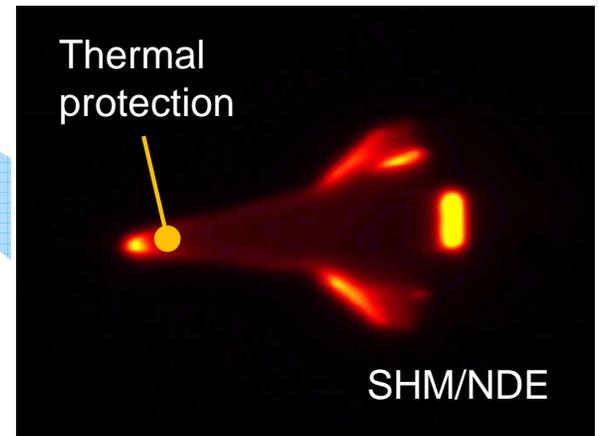
*In-space operation*

Thermal management



Thermal protection

SHM/NDE



*Re-entry*

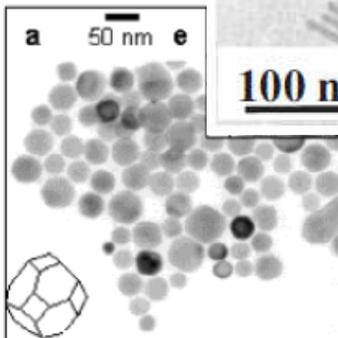
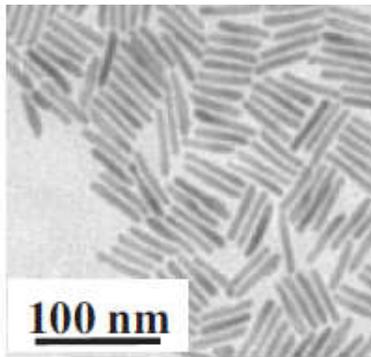
- Extreme environment
- Light-weight

# Challenges of Engineered Materials

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



[Peng. Adv. Mat.,  
2003]



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

## Aero/astro structures [meters]

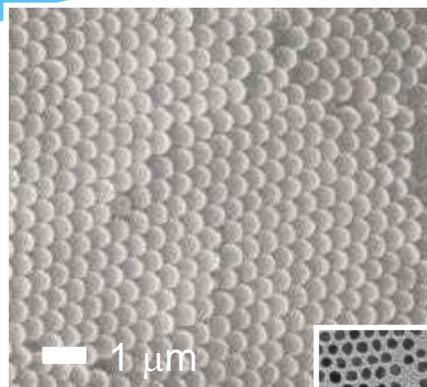


[NASA]

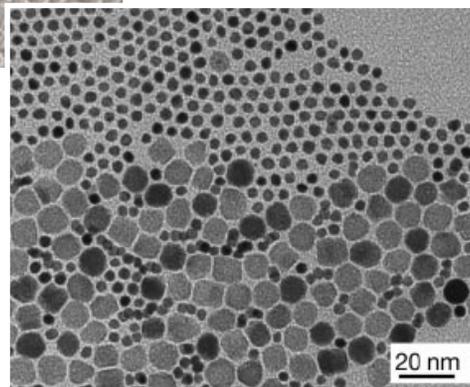


- **Missing scalable manufacturing**
- **Poor property scaling**

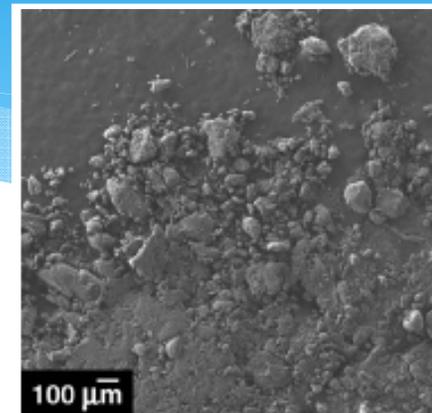
# Challenge: Manufacturing



[Velve, Science, 2000]

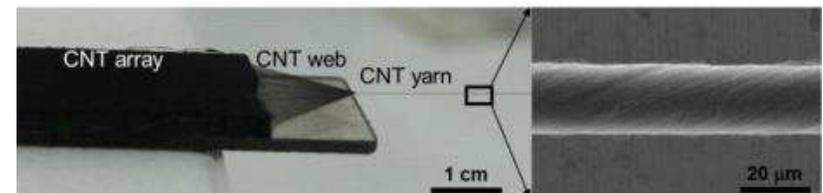
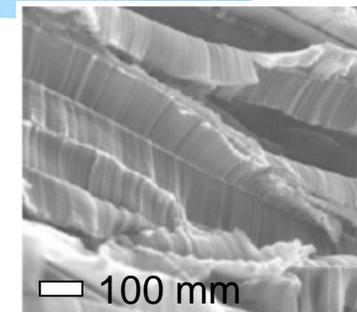


[Zeng, Nature Letter, 2002]



[Thostenson et al., Carbon, 2006]

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



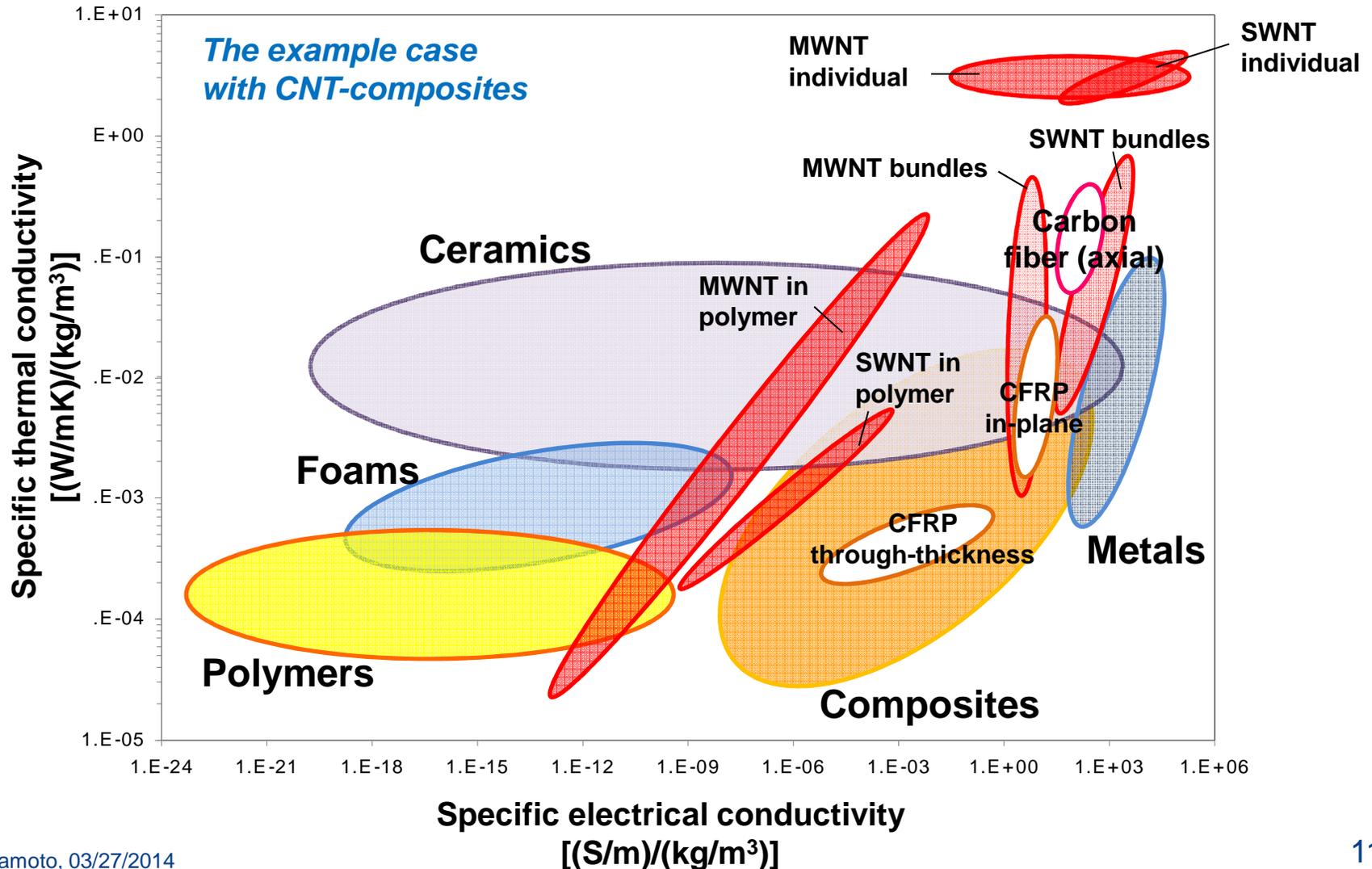
[Ghemes et al., Carbon, 2012]

## Nano-particle assembly

## Mixing of nano-particles into matrices



# Challenge: Property Scaling



# Key Technology Steps

... to apply **bulk** engineered materials with **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

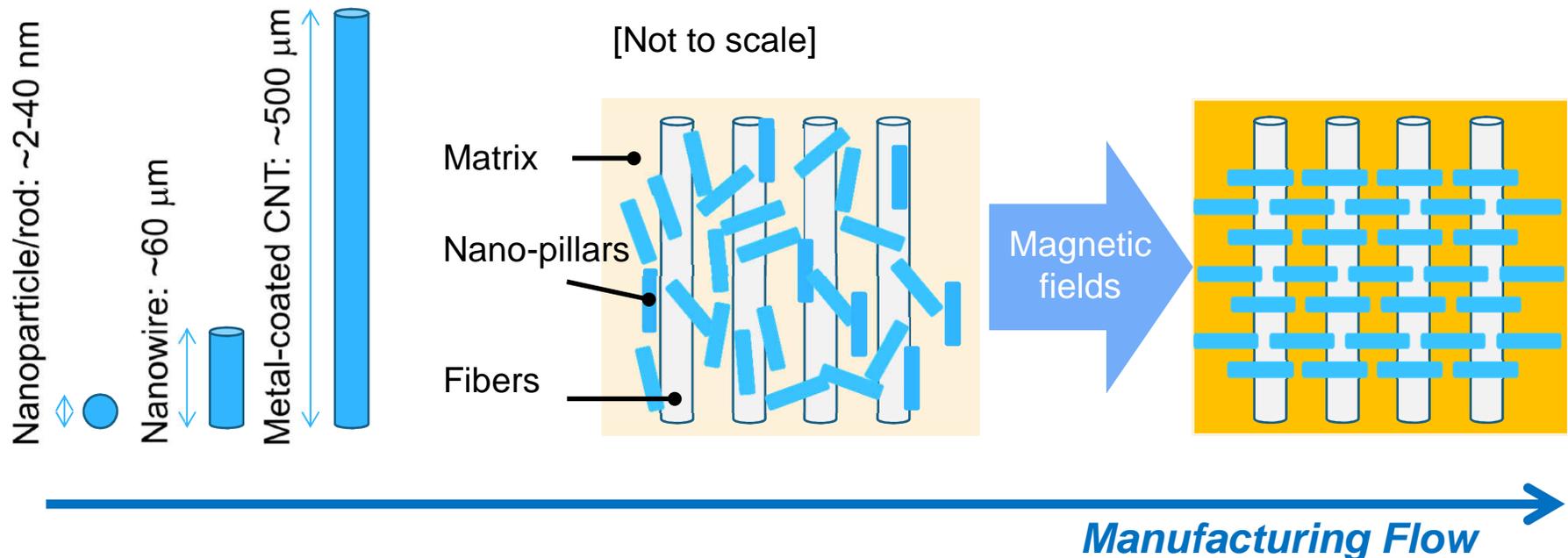
- Meso-scale
- Intrinsic anisotropy

## Micro-Structuring

Control by external fields

## Compositing

- Bulk processing
- Scalability

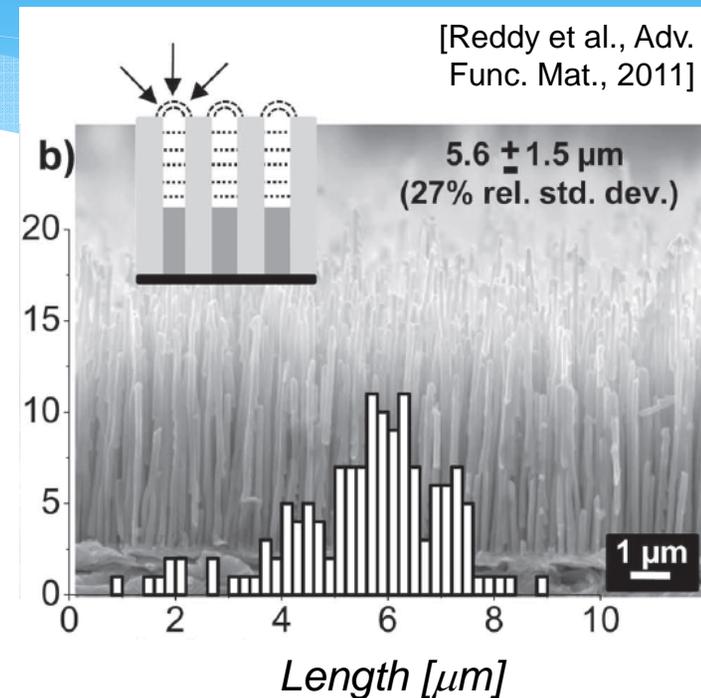
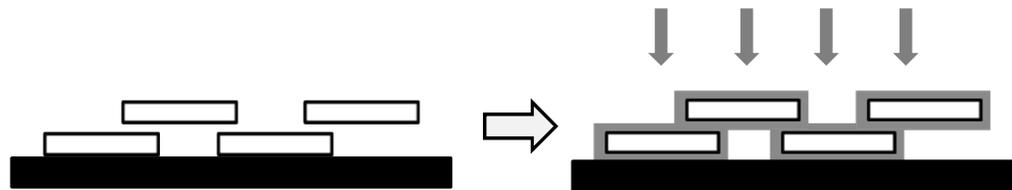
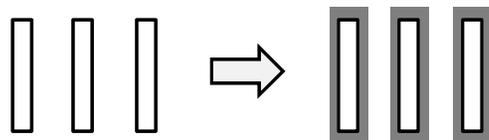


# Technical Approach

- ***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

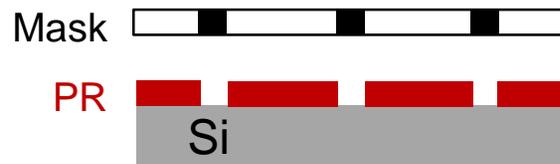
- Previously: metal deposition on porous templates
  - Aspect ratio:  $\sim 100$
- Novel fabrication: **conformal coating of CNTs with ferromagnetic metals**
  - High aspect ratio ( $\sim 1000$ )
  - Bulk fabrication



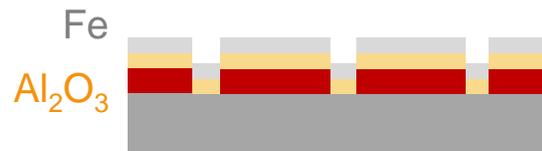
# Fabrication of Magnetic Nano-Pillars (continued)

## 1. Patterning of catalyst

Photolithography using image reversal photoresist



E-beam metal dep:  
Al<sub>2</sub>O<sub>3</sub> 30nm, and Fe 30 nm

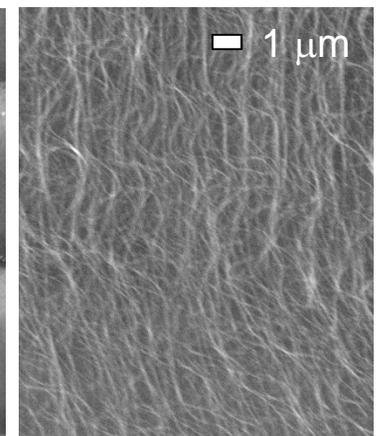
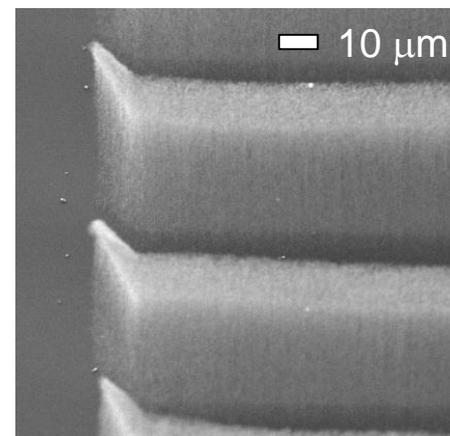
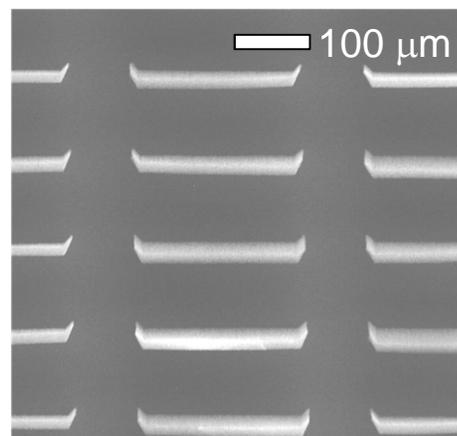
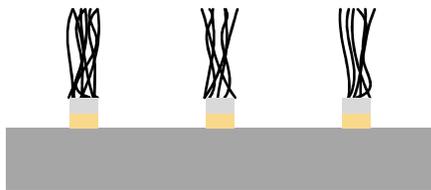


Lift-off



## 2. Chemical vapor deposition of aligned CNTs

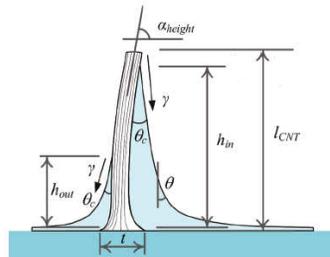
Ethylene/Ar introduction  
at 750°C



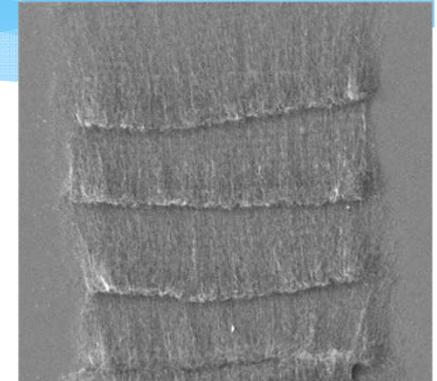
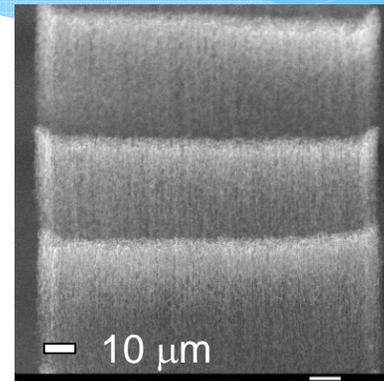
# Fabrication of Magnetic Nano-Pillars (continued)

## 3. Controlled laying of CNTs

Directional collapse by capillary forces

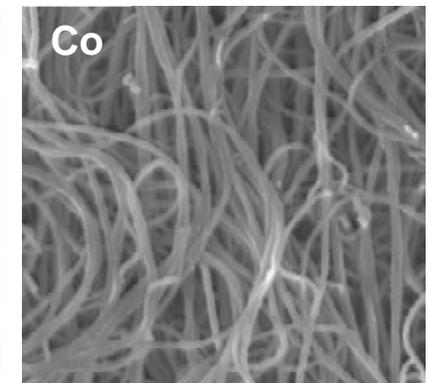
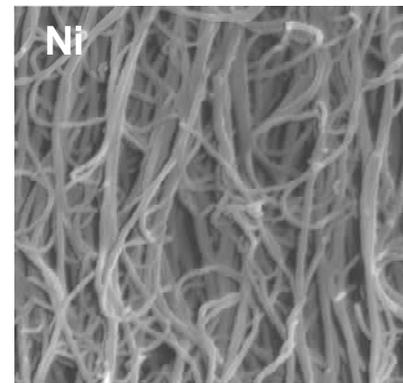
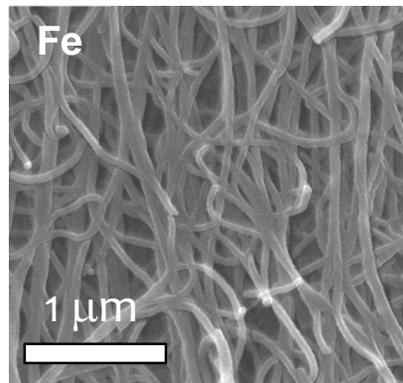
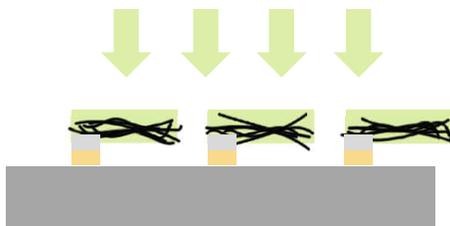


[Tawfik et al, Langmuir, 2011]

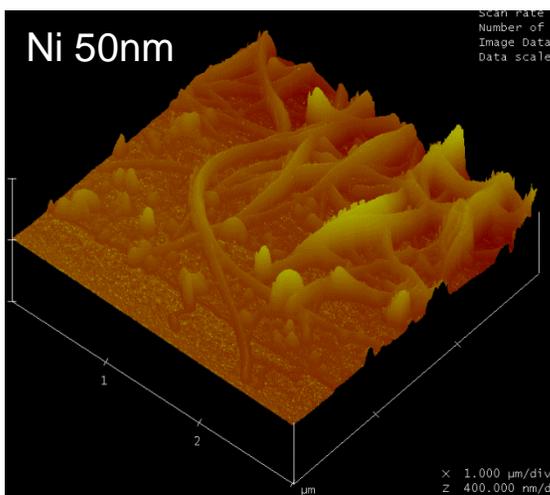
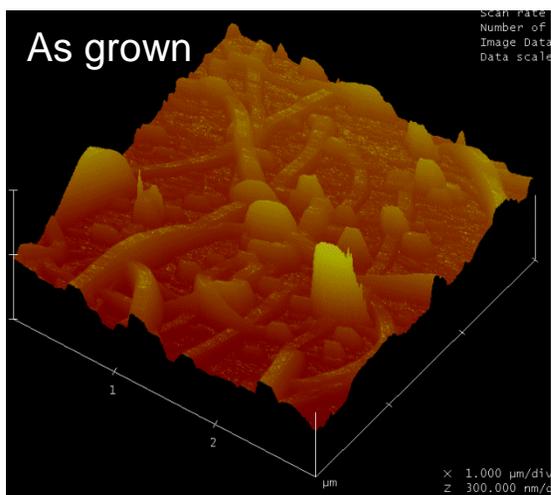
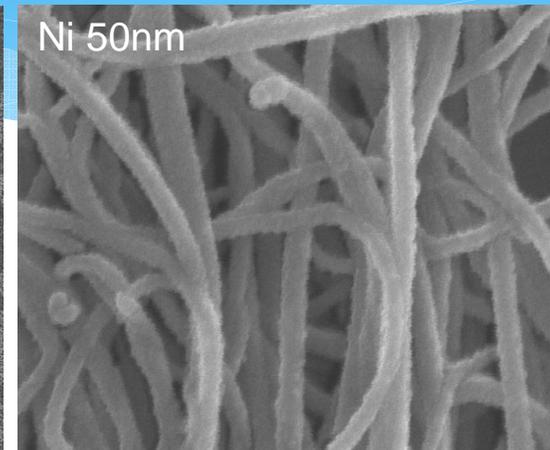
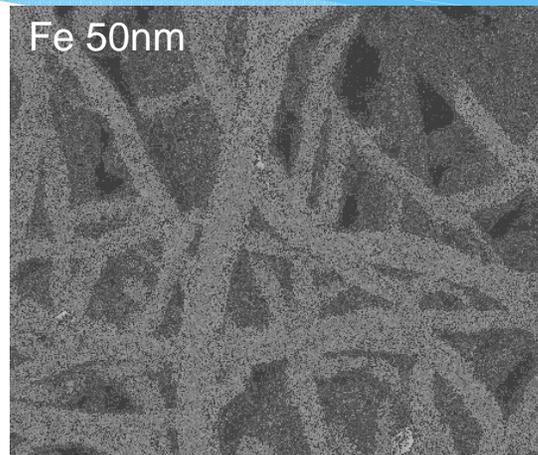
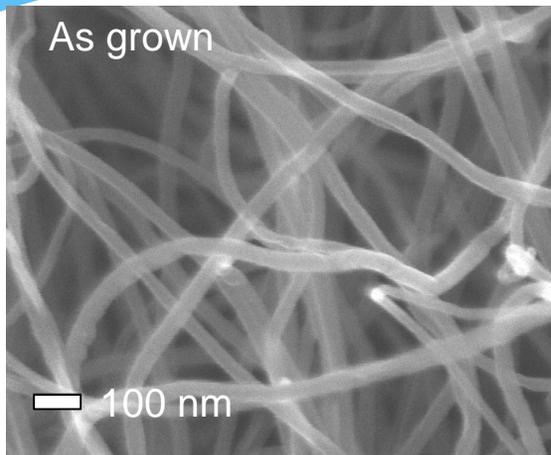


## 4. E-beam deposition of metals

- Fe, Ni, and Co
- Thickness: ~50nm



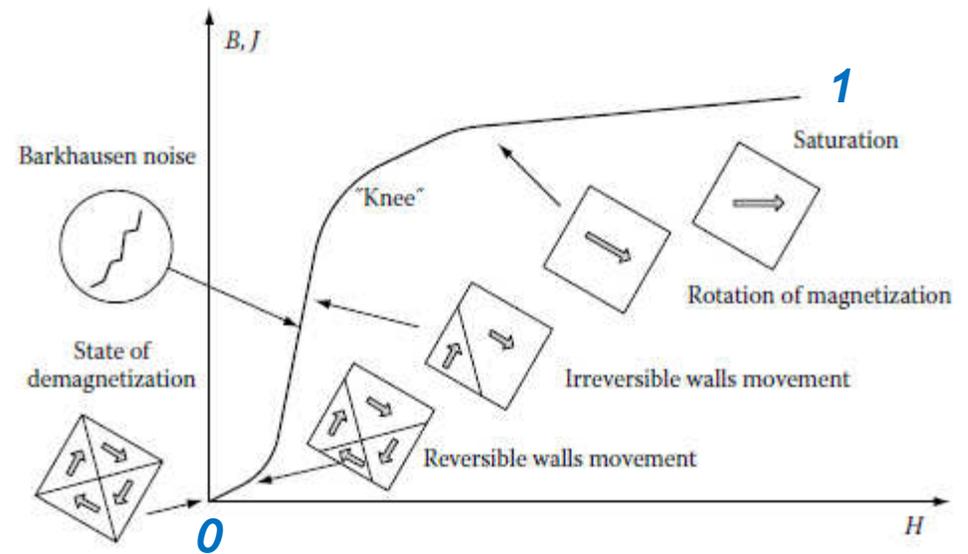
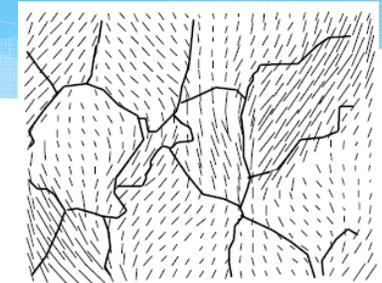
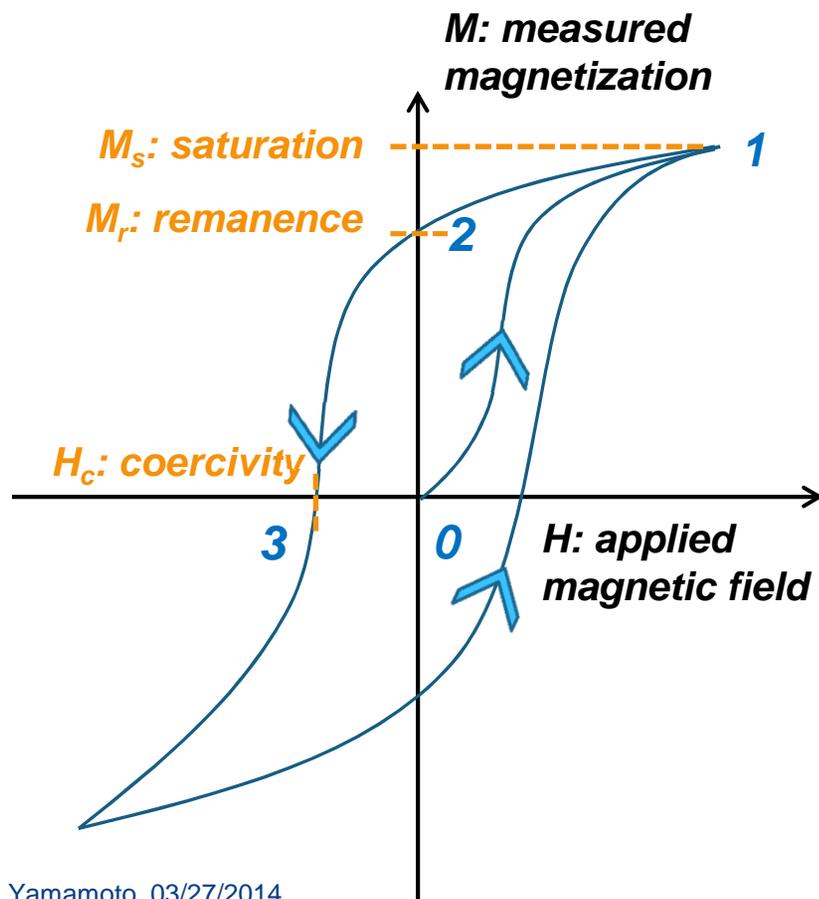
# Inspection of Fabricated Nano-Pillars: Metal Coating



- SEM: visual inspection of conformal coating
- AFM: metal-coated CNTs  $\sim 30\text{-}85\text{nm}$  vs. as-grown CNTs  $\sim 20\text{-}55\text{nm}$

# Magnetization of Ferromagnetic Materials

## Hysteresis loop

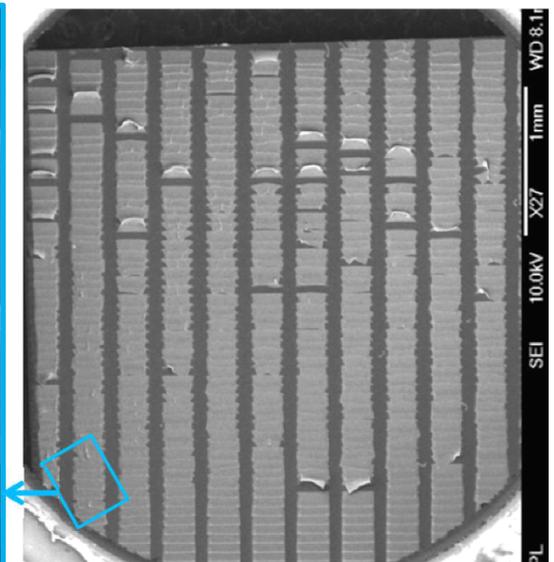
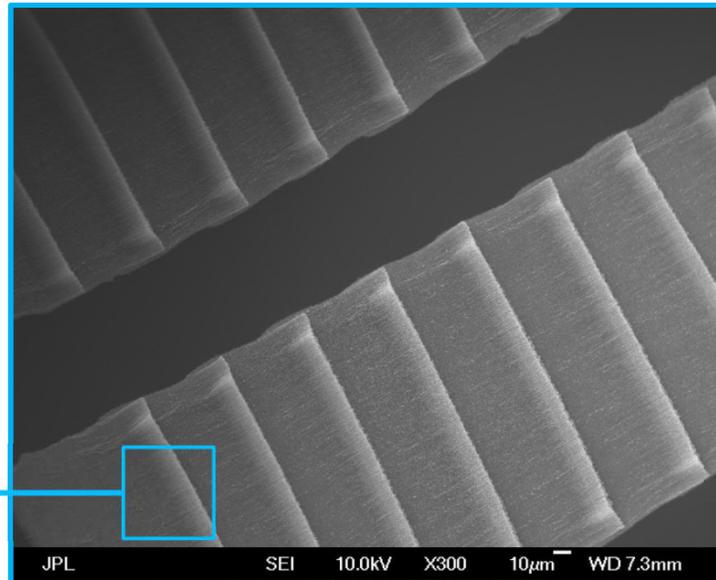
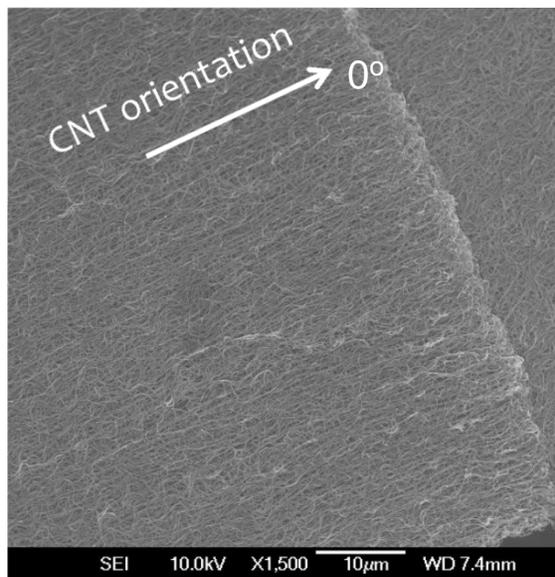
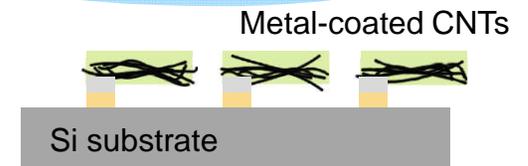




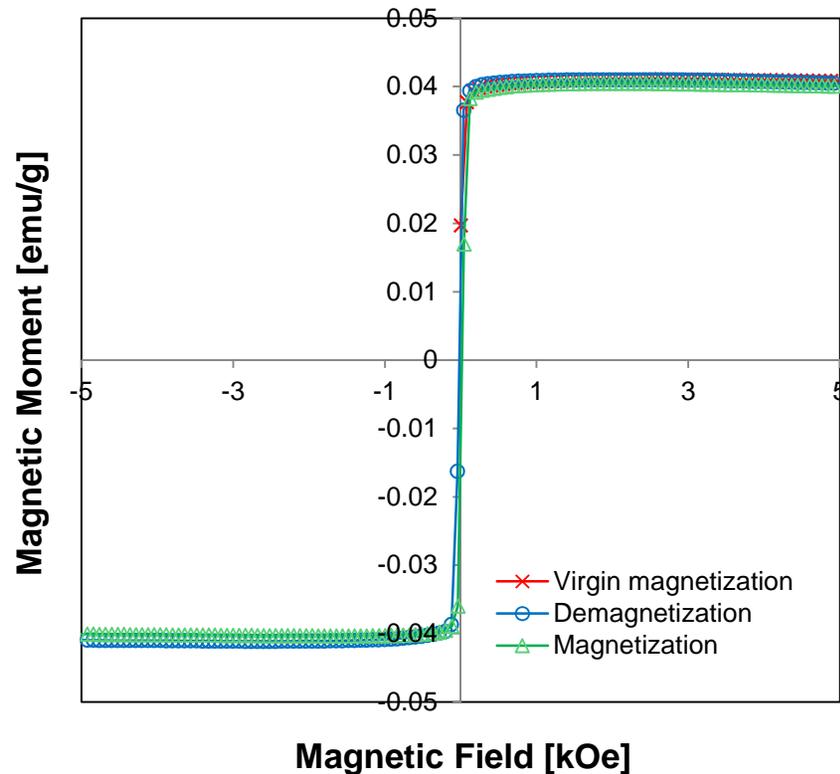
# Magnetic Characterization: Nano-Pillar Samples



- 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



# Measured Magnetic Properties: Fe Baseline

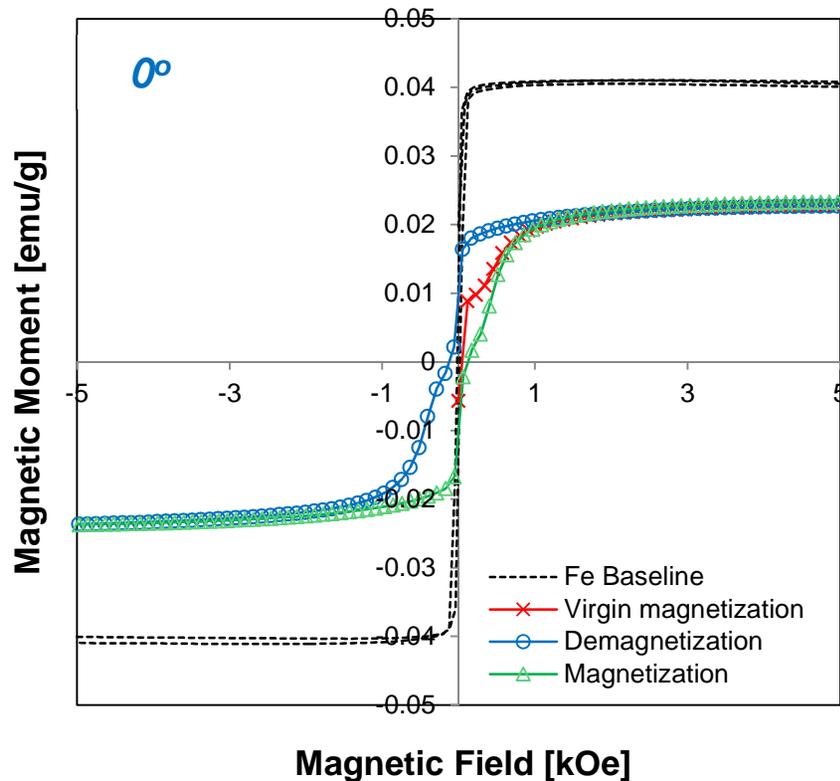
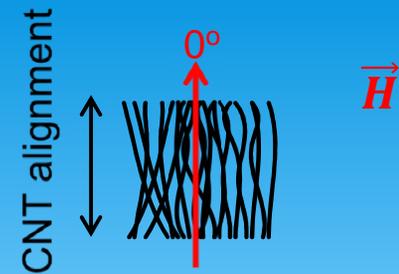


- Ferromagnetic
- Small hysteresis
- Coercivity: comparable and slightly higher, due to impurities or stresses

	Sample	Hc [Oe]
Measurement	Fe 50nm on Si	11.1
Literature	Iron, high purity	0.15
	Armco iron	1.0
	Cast iron (annealed)	5

[Kaye & Laby, Table of Physical & Chemical Constants]

# Measured Magnetic Properties: Fe-Coated CNTs

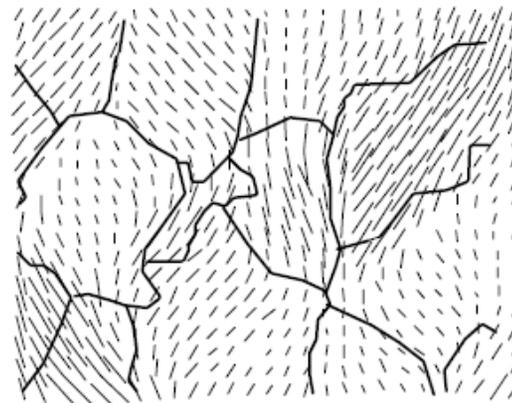
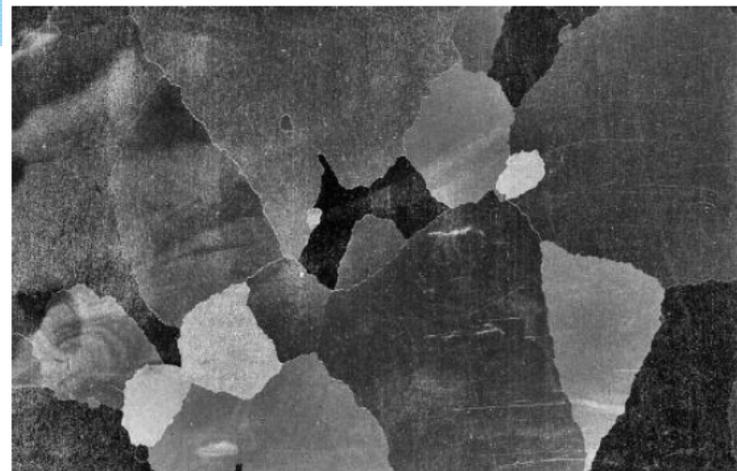


- Ferromagnetic
- Different from Fe baseline
  - Magnetic moment without  $H$
  - Hysteresis
  - Higher coercivity and remanence
  - Lower saturation
  - 2 phases

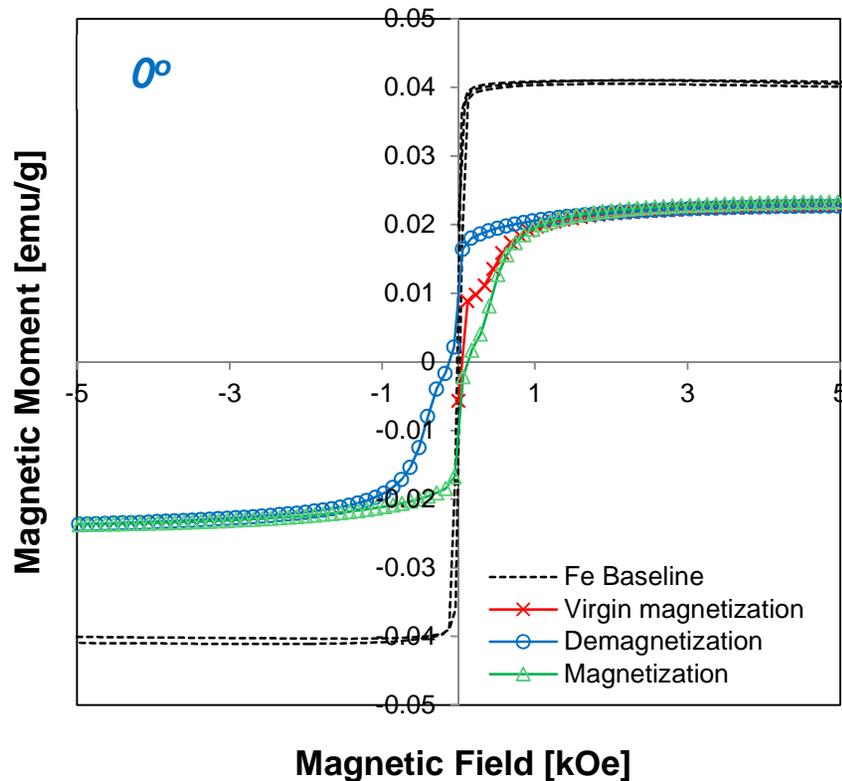
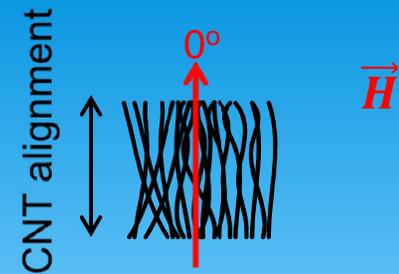
# Magnetization of Ferromagnetic Materials

## *Magnetic domain structure*

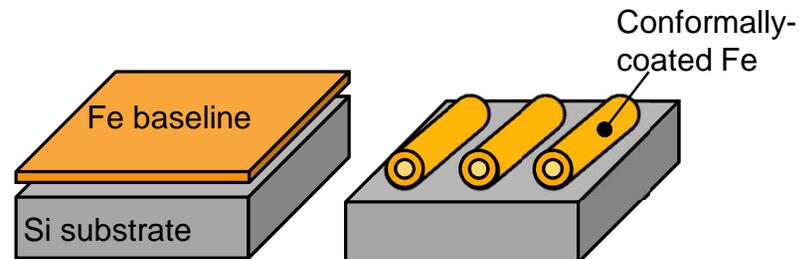
- Polycrystallites (grains), each with a certain magnetization direction
- Local magnetization depends on
  - Grain structure, size
  - Presence of impurities
  - Local stress
  - Balance of local energy
- Formation of magnetic domains through minimization of free energy



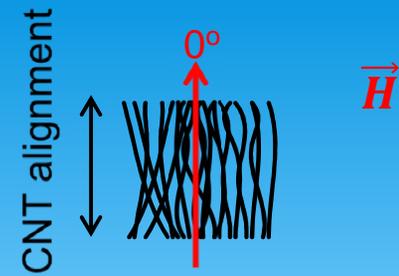
# Measured Magnetic Properties: Fe-Coated CNTs (continued)



- 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?

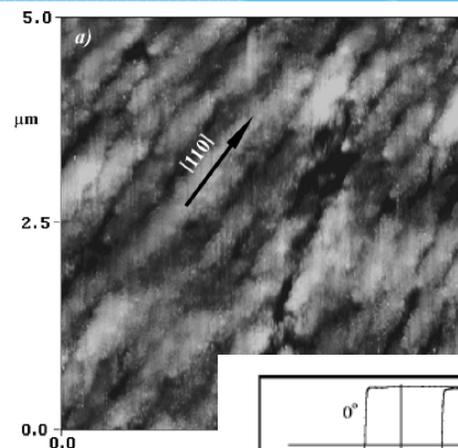
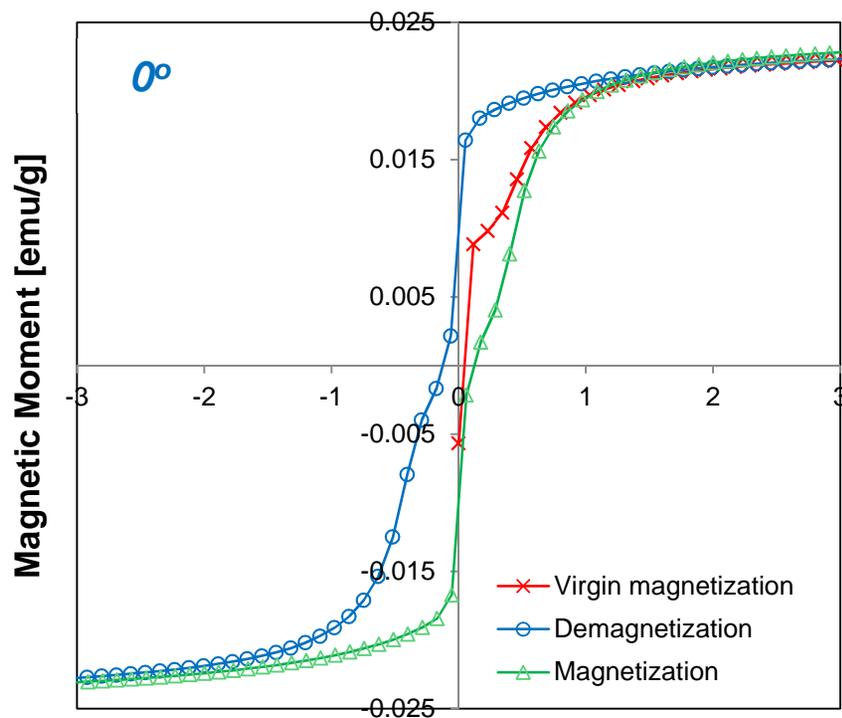


# Measured Magnetic Properties: Fe-Coated CNTs (continued)

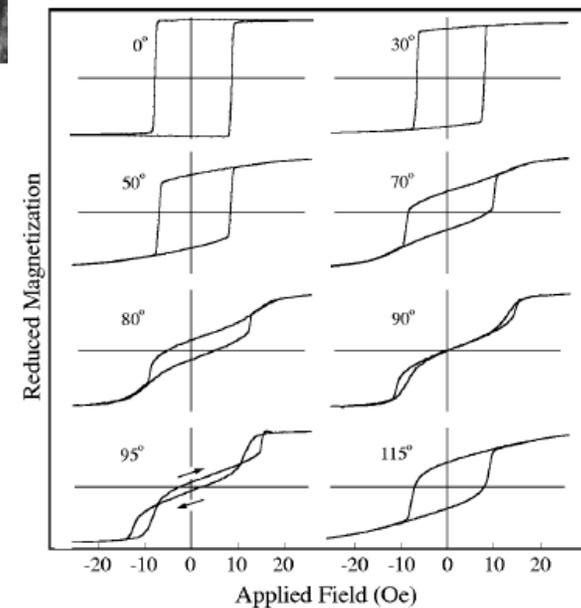


2 phases observed at the 0° angle

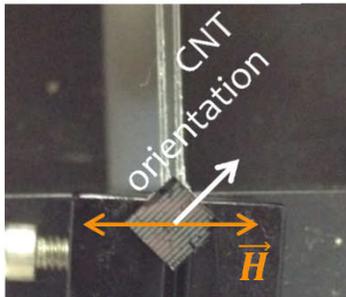
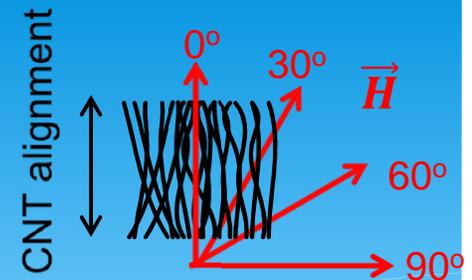
- Mismatch between crystalline and CNT orientations
- CNT misalignments



6-nm-thick Fe film grown on Si (111) [Cougo dos Santos et al., Phys. Rev. B, 2000]

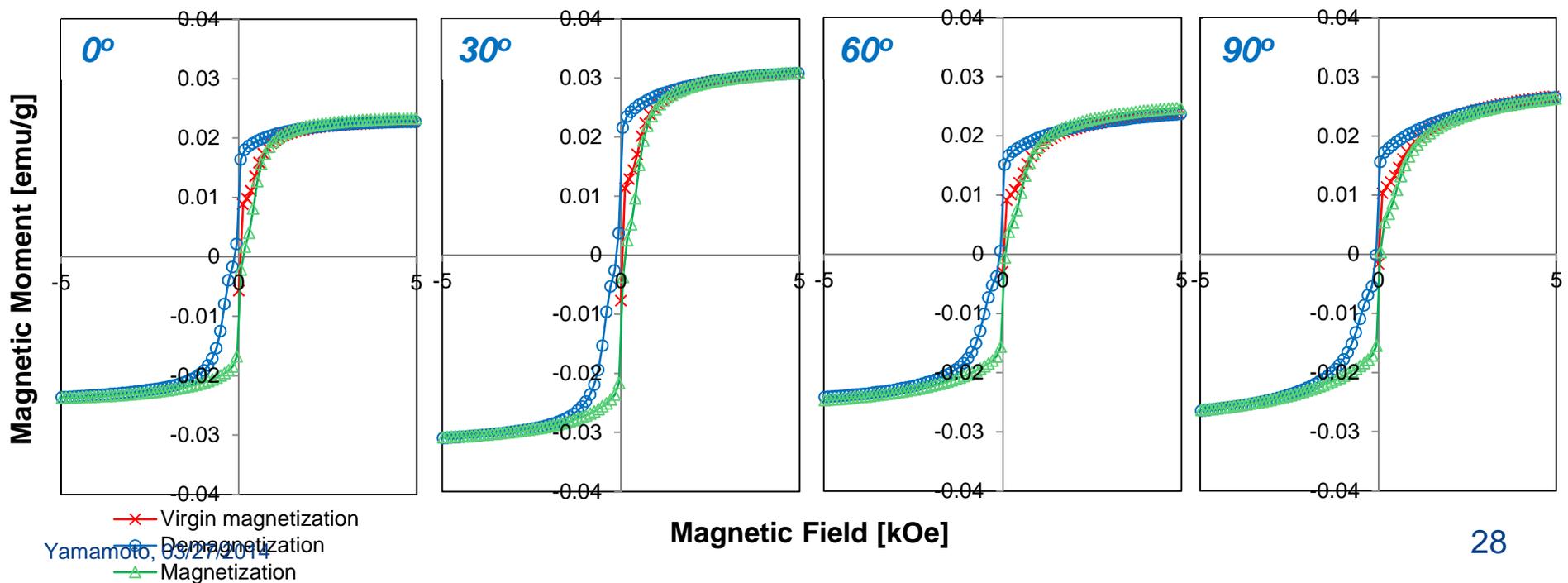


# Measured Magnetic Properties: Fe-Coated CNTs (continued)

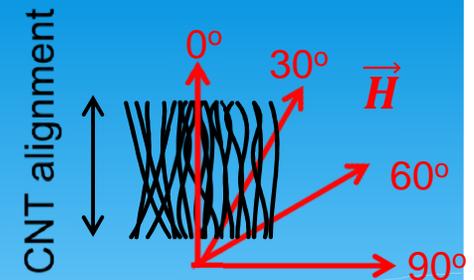


Measurement with the samples oriented against  $H$  at an angle

- 2 phases observed regardless of the directions
- Slight shifting of coercivity, saturation, and remanence

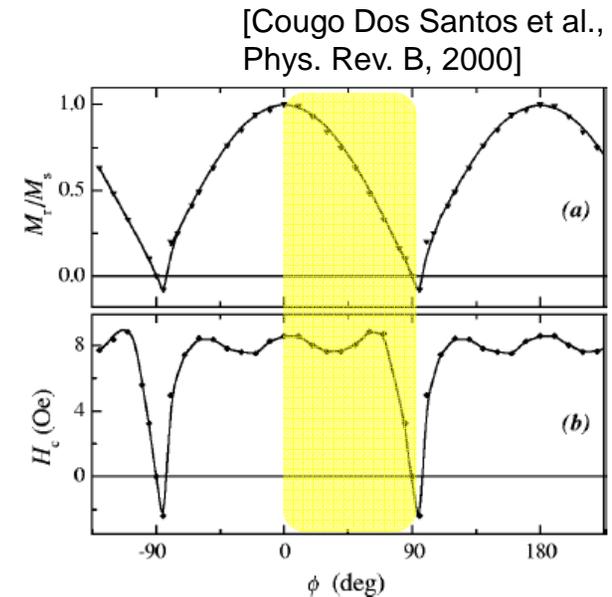
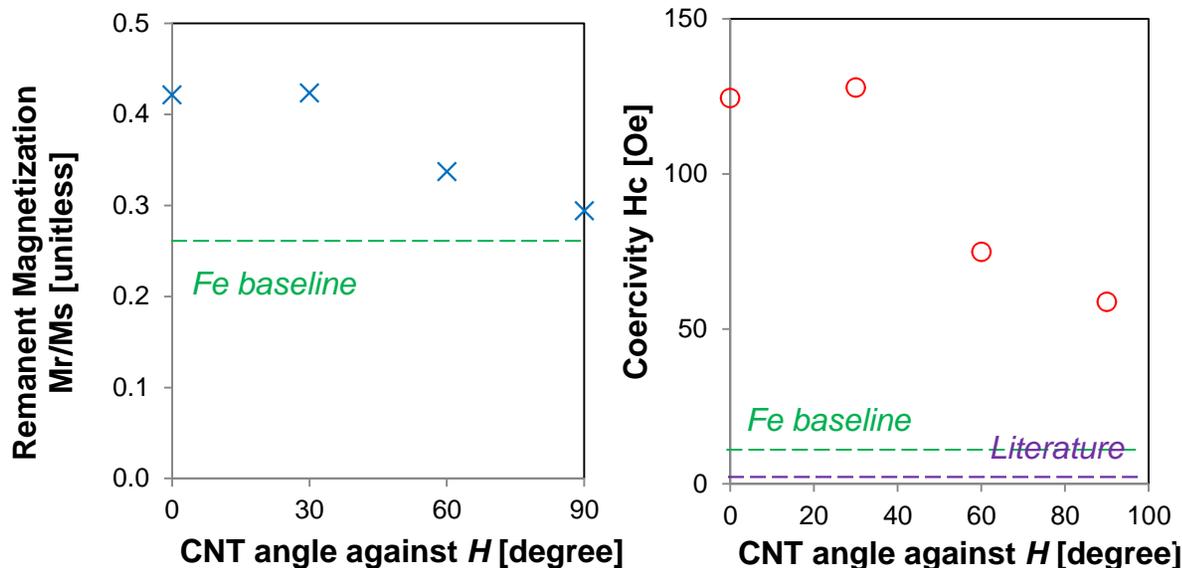


# Measured Magnetic Properties: Fe-Coated CNTs (continued)

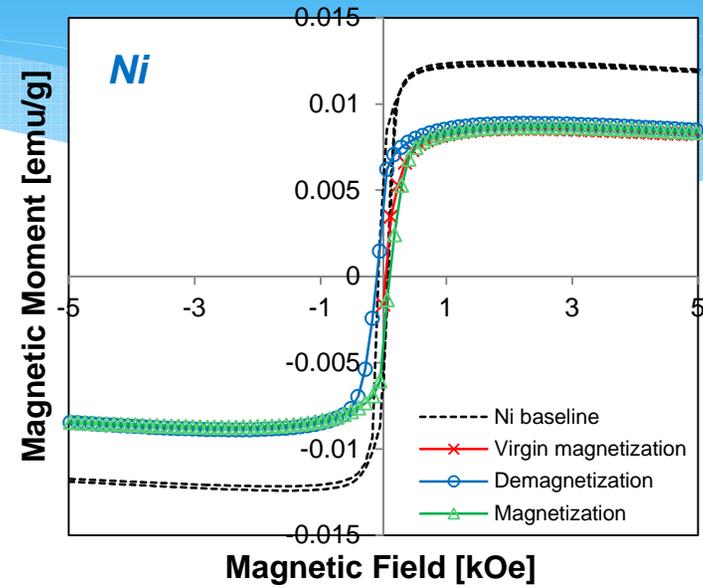
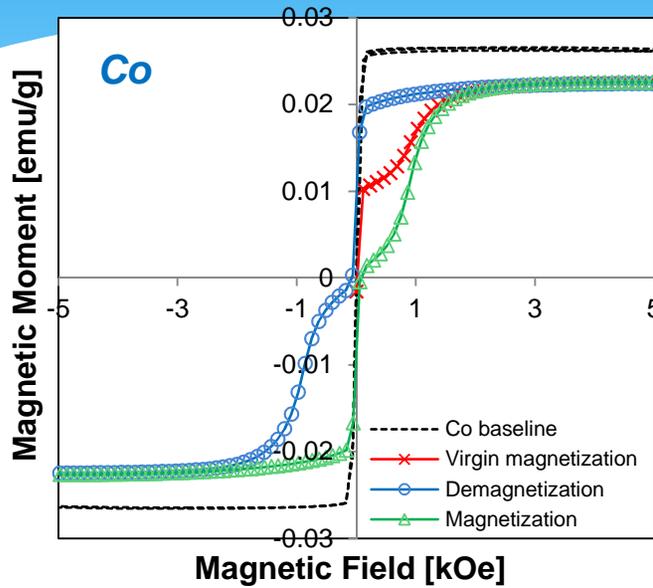


## Dominant effect of micro-structure anisotropy

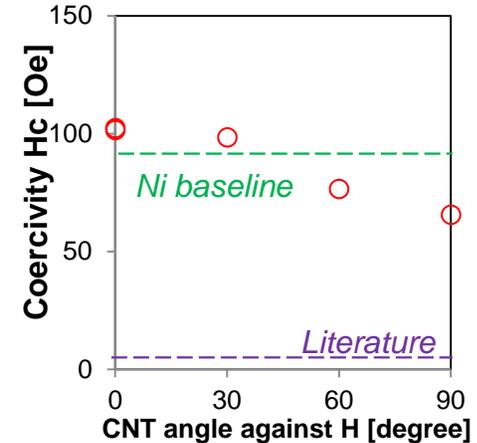
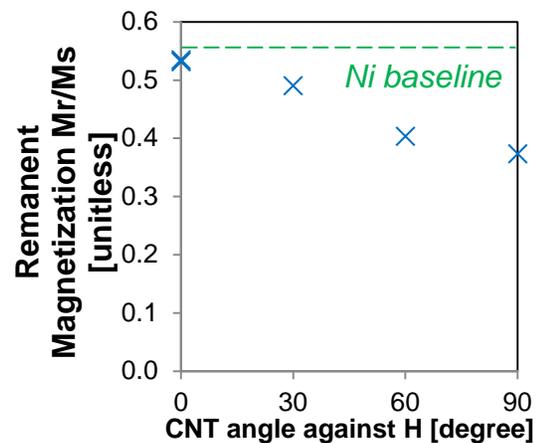
- Both reduced remanent magnetization and coercivity decrease with the sample angle



# Measured Magnetic Properties: Co-Coated and Ni-Coated CNTs



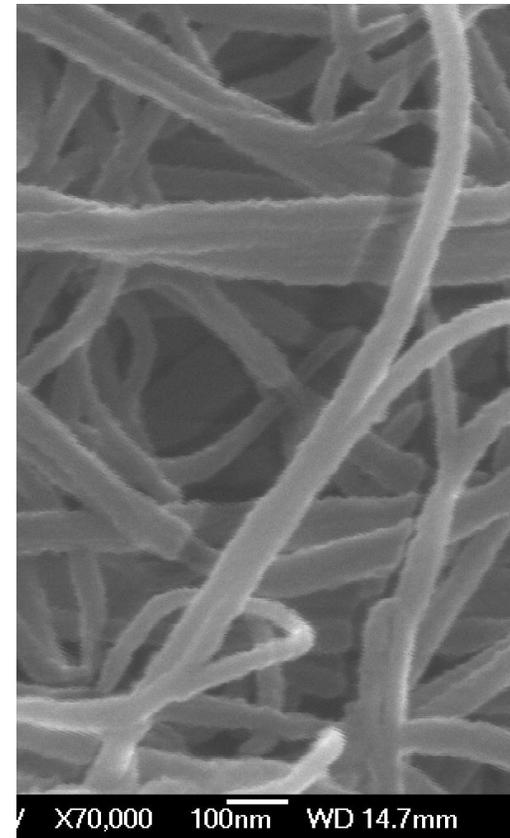
- Co-coated CNTs: trends comparable with Fe, more defined 2phase
- Ni-coated CNTs
  - Minimal hysteresis
  - Coercivity and remanence comparable with baseline



# Progress Summary: Magnetic Assembly of Nano-Pillars

## *Fabrication of magnetic nano-pillars*

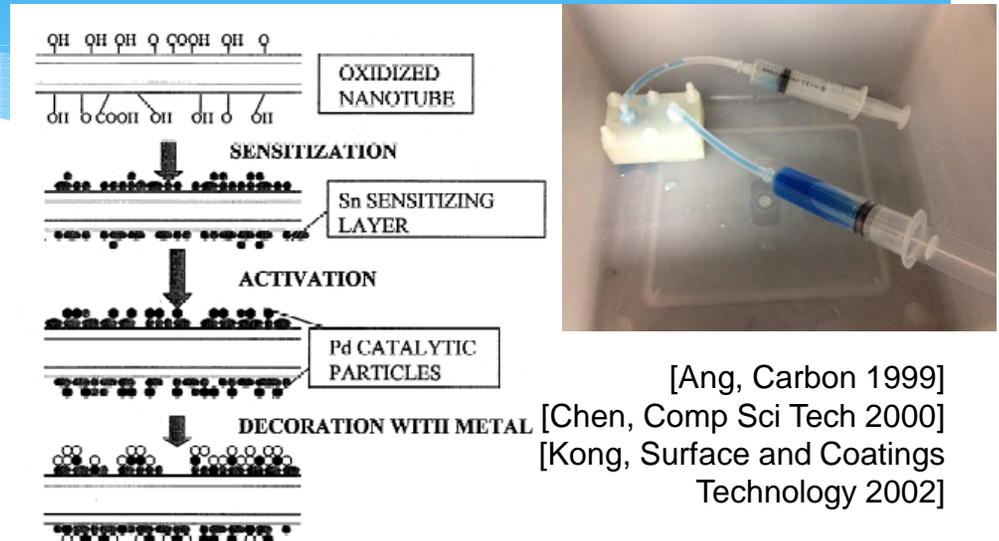
- Established a simple fabrication method
  - High aspect ratio using CNT templates.
  - Conformal coating and scalability to be improved
- Evaluating the effects on magnetic properties from
  - Grains/domains: hysteresis
  - Micro-structuring: anisotropy
  - Metal-CNT binding/interfaces



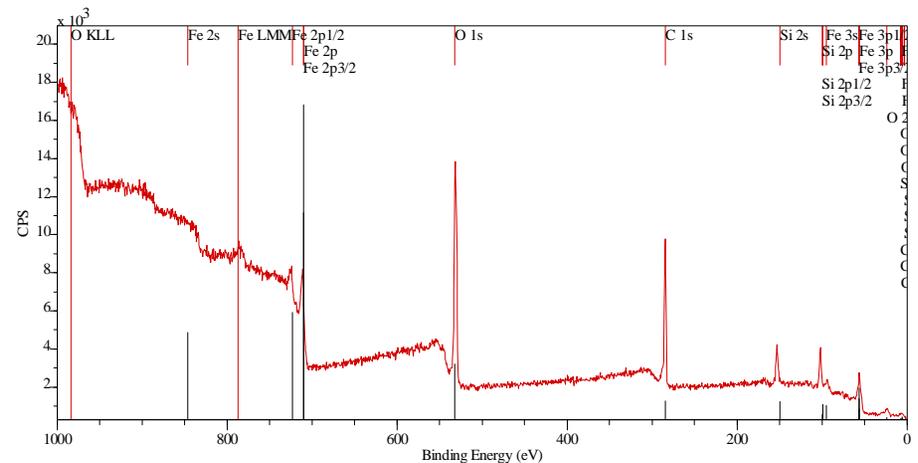
Research Efforts to be Continued

# 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)

- 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

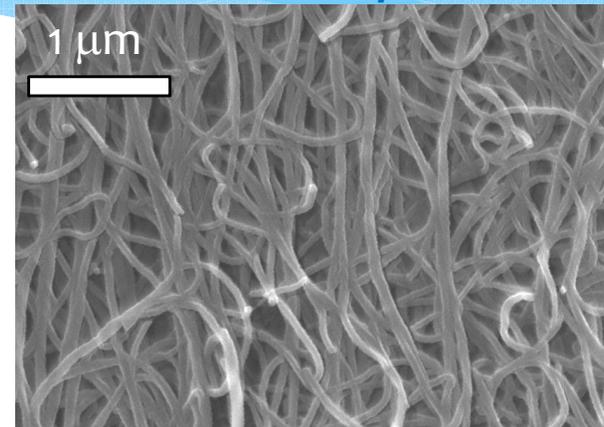


[Rotello, Nanoparticles: Building Blocks for Nanotechnology, Kluwer Academic Publishers, 2004]

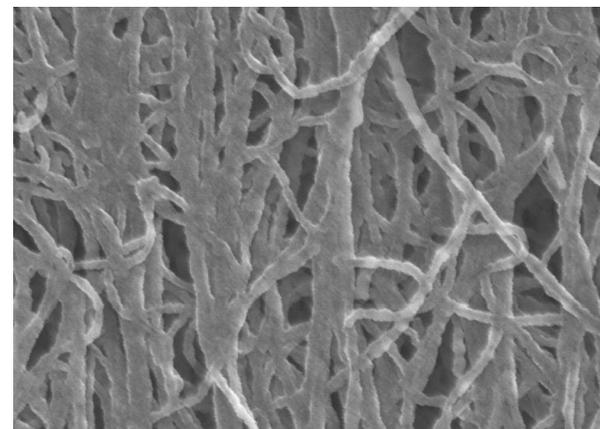
# Research Plan: Magnetic Assembly of Nano-Pillars (continued)

- 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

*Fe 50nm as deposited*



*After sintered*



# Future Research Plan: Scalable Manufacturing

