Carbon Nanotubes/Polymer Nanocomposites

-- From Fundamental to Application

Professor Peng-Cheng MA

mapc@ms.xjb.ac.cn

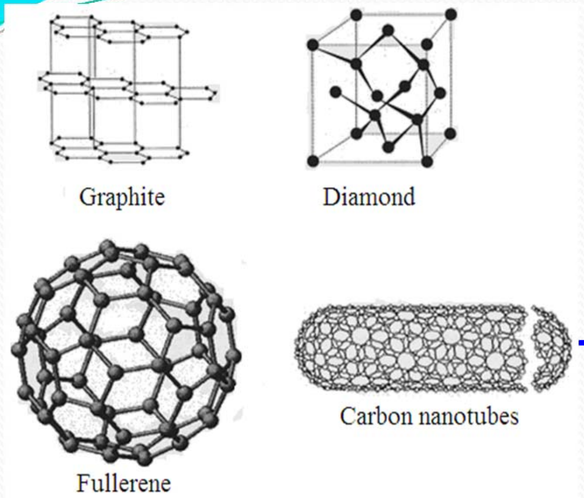
The Xinjiang Technical Institute of Physics and Chemistry,

Chinese Academy of Science, Urumqi, 830011, China

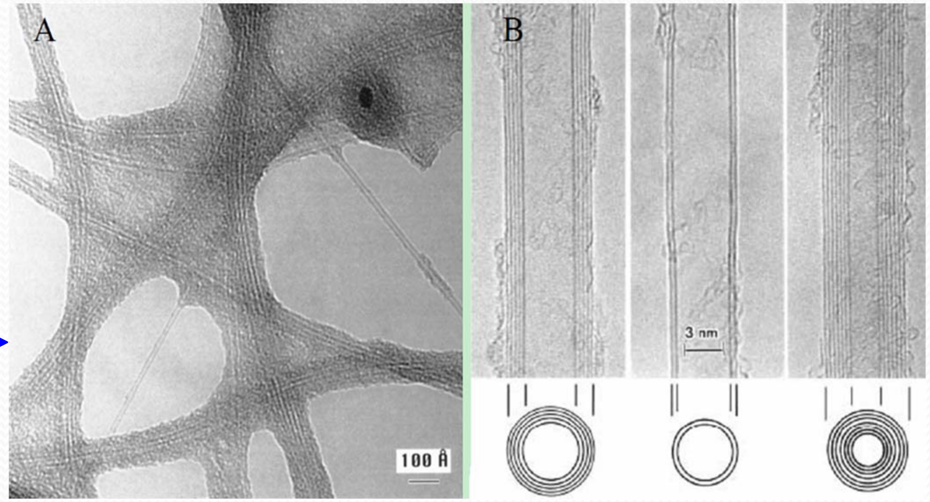
Outline

- **Introduction**
  - -- What are carbon nanotubes (CNTs)?
  - -- Properties of CNTs
  - -- Research objectives
- **Fundamental issues of CNT/polymer nanocomposites**
  - -- CNT functionalization
  - -- CNT dispersion
  - -- Nanocomposites reinforced by CNT foam
  - -- Ag@CNT/polymer nanocomposites
  - -- Electrically conducting nanocomposites
- **Engineering application of CNT/polymer nanocomposites**
  - -- Perspectives for wind blade materials
  - -- Sensory materials for defect monitoring in FRPs
- **Concluding Remarks**

CNTs and their Properties



Different carbon materials



Carbon nanotubes (A: SWCNTs; B: MWCNTs)

Cylinders composed of graphene layers with diameters in nanometer scale

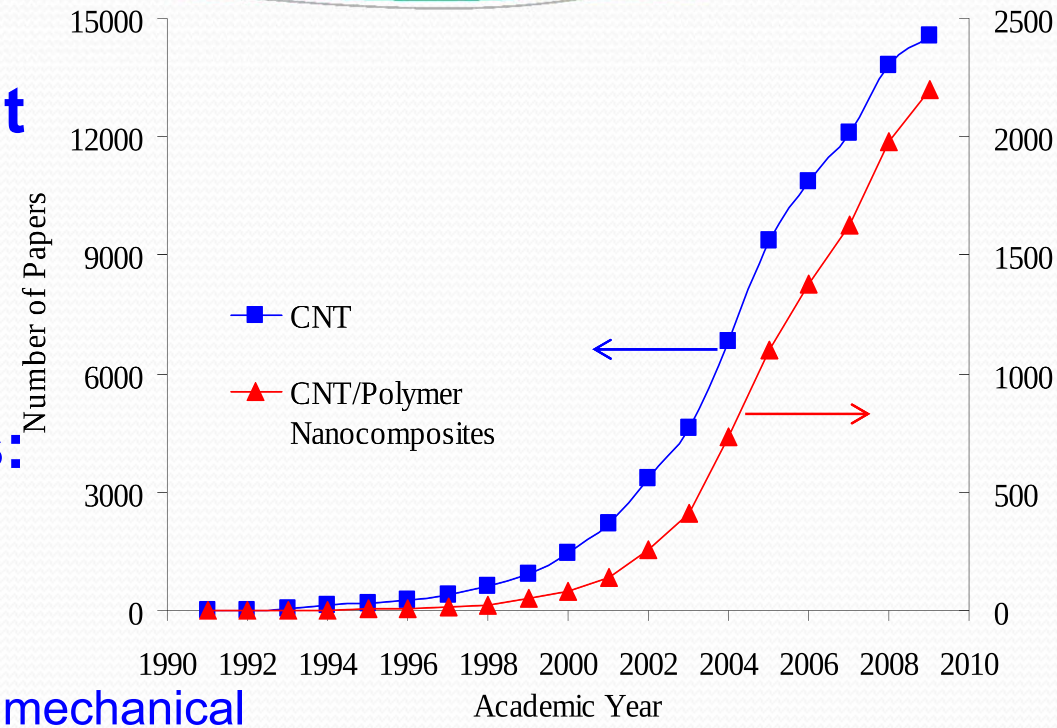
➢ Properties of CNTs

Material	ρ(g/cm³)	EC (S/cm)	TC (W/m·K)	CTE	E (GPa)
Graphite	1.9-2.3	4000*, 3.3**	298* 2.2**	-1.2×10^{-6}* 25.9×10^{-6}**	1000* 36.5**
Diamond	3.5	10^{-2}	900-2320	$1\sim3\times10^{-6}$	500~1000
C_{60}	1.7	10^{-5}	0.4	6.2×10^{-5}	14
SWNTs	0.8	$10^{2}\sim10^{6}$	~6000	Negligible	1000
MWNTs	1.8	$10^{3}\sim10^{5}$	~2000	Negligible	1000

*: in-plane; **: c-axis.

CNT/Polymer Nanocomposites

- **CNTs: Ideal reinforcement for polymer composites**.
  -- Thermoplastic matrix: PE, PP…
  -- Thermosetting matrix: EP, PU…



- **CNT/polymer composites: Exceptional properties for different applications**

  -- **Structural composites**: Excellent mechanical properties of CNTs (High modulus, strength and strain to fracture);
  -- **Functional composites**: Multi-functional characteristics of CNTs (Electrical, thermal, optical along with mechanical properties).

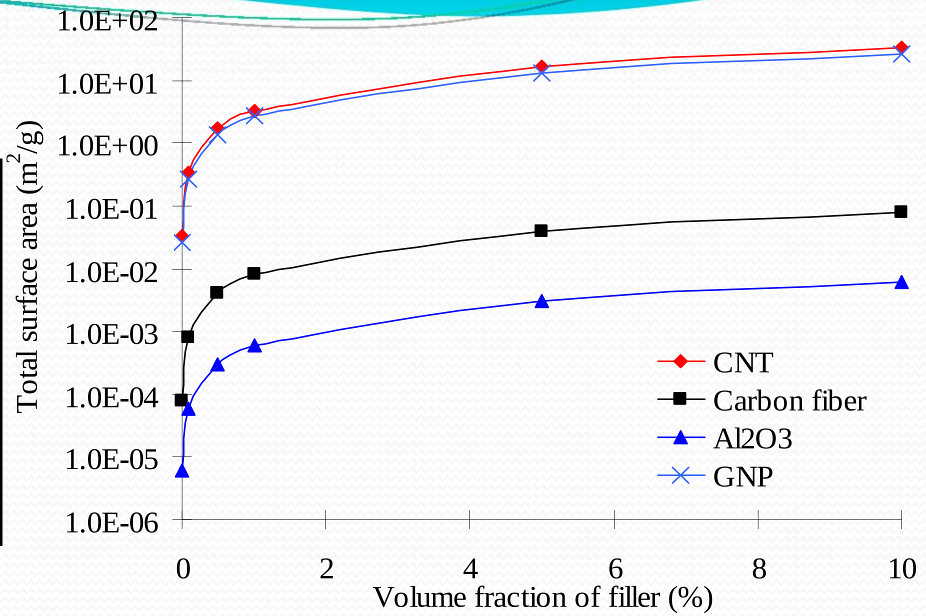
- **Prerequisites for excellent properties of CNT/polymer composites**
  -- **Perfect dispersion** of CNT in matrix
  -- **Good interfacial interaction** between CNT and matrix

Dispersion of CNT in Polymer Matrix

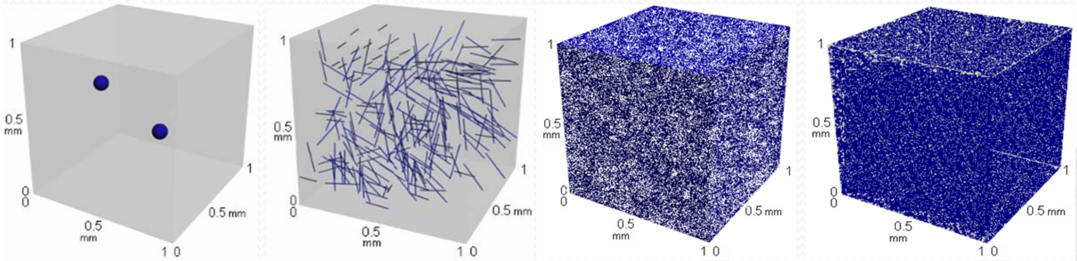
➢ Number of fillers in matrix

Filler	Dimension of filler	Particles*
Al_2O_3	d=100 μm	1.9
CF	d=5μm, l= 200 μm	255
GNP	l=w= 45μm, t= 7.5nm	6.58×10^4
CNT	d=12 nm, l= 20 μm	**4.42×10^8**

* In $1mm^3$ with 0.1 vol% filler content



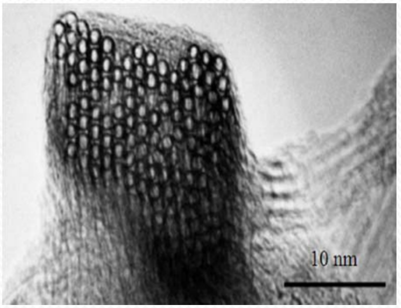
➢ **Large quantity** of CNTs & size effect lead to an large surface area

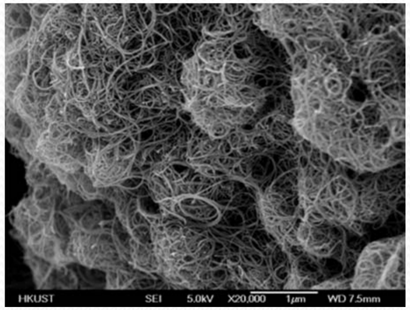


Al_2O_3 C fiber GNP CNT

➢ **Distribution** of micro-filler is more uniform than that of nano-fillers in matrix

➢ CNT agglomeration





As-produced CNTs are held together in bundles

CNT Functionalization

- **Why functionalization?**

  -- Inherently inert nature of C on CNTs, weak load transfer across the CNT/matrix interface.

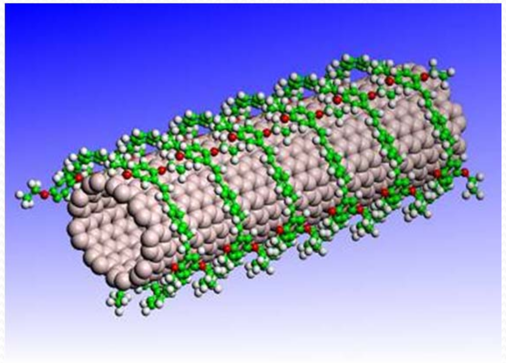
- **Methods for CNT functionalization**

  Covalent method: Covalent linkage of functional entities on CNTs.

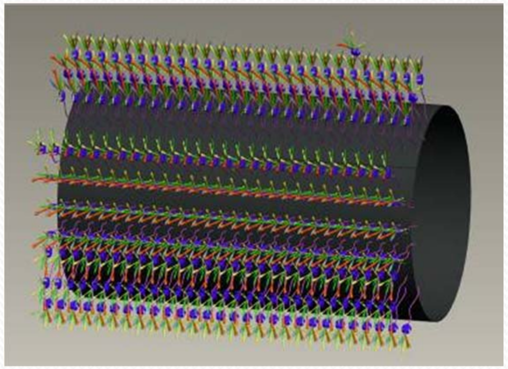
  -- Side-wall functionalization: $sp^2 \rightarrow sp^3$ and a loss of π electrons on CNT graphene layer .

  -- Defect functionalization: Chemical transformation of defects (open end, pentagon irregularities on CNT) to stable groups(-OH, -COOH, etc)

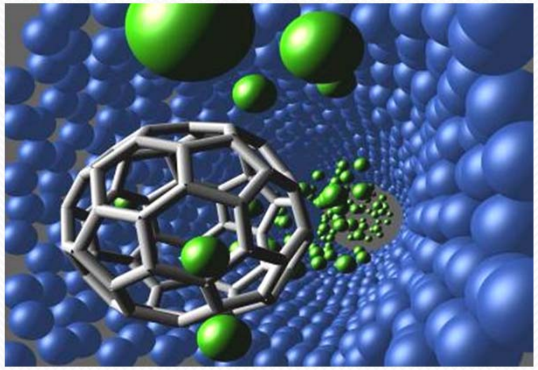
  Non-covalent methods



Polymer wrapping



Surfactant adsorption



Endohedral method

Advantages & Disadvantages of Methods for CNT Functionalization

Method		Principle	CNT damage	Easy to use	Interaction with matrix*	CNT Agglomer.
Covalent method	Side wall	Hybridization change of C from sp^2 to sp^3	√	×	S	√
	Defect	Defect transformation	√	√	S	√
Non-covalent method	Polymer wrapping	Van der Waals force, π-π stacking	×	√	V	×
	Surfactant adsorption	Physical adsorption	×	√	W	×
	Endohedral method	Capillary effect	×	×	W	√

*S: Strong; W: Weak;
V: Variable according to the miscibility between matrix and polymer on CNT.

Objectives of Research

- **Novel surface treatment techniques** to promote CNTs dispersion and interfacial adhesion with polymers

- **Fundamental issues on CNT/polymer nanocomposites**
  -- Dispersion and evaluation
  -- Correlation between dispersion and functionalization of CNTs
  -- Effect of dispersion and functionalization on properties of CNT/polymer nanocomposites
  -- Behaviour of load transfer from matrix to CNTs

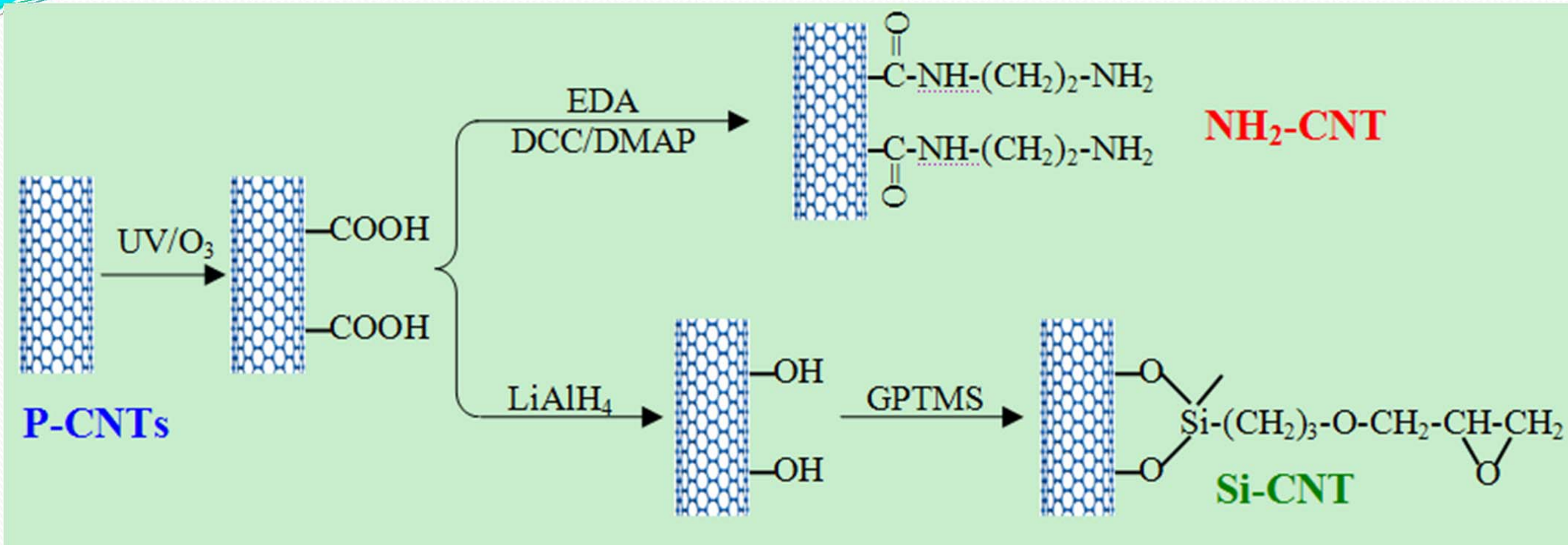
- **Application of CNT-reinforced nanocomposite**
  -- Multi-functional properties
  -- Synergic benefits
  -- Reducing the production cost

Fundamental issues of CNT/polymer nanocomposites

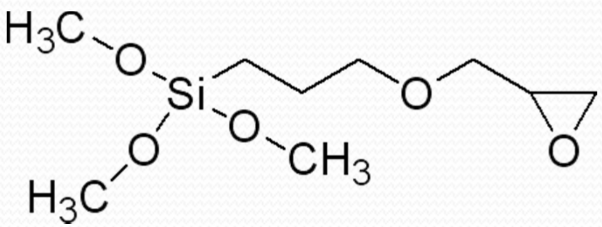
Functionalization of CNTs

- **Methods for functionalization**
- **Effect of functionalization on properties of CNT/polymer nanocomposites**
- **Behavior of load transfer in functionalized CNT/polymer nanocomposites**
- **Behavior of dispersed CNTs in matrix during processing**

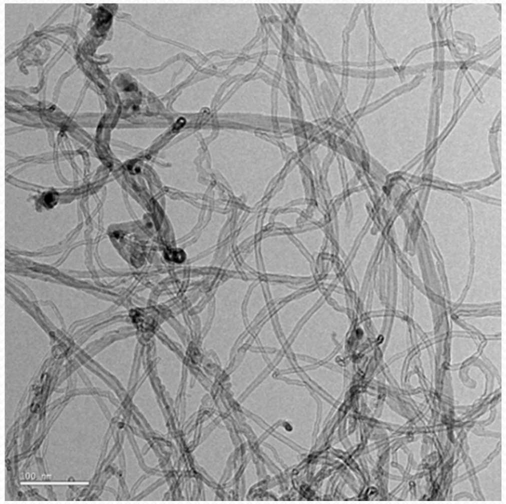
CNT Functionalization



- **Amino**: Ethylene diamine (EDA) with of DCC (dicyclohexylcarbodiimide) and DMAP (dimethylamino-pyridine)
- **Silane**: GPTMS



- **CNTs used in this study**



-- Multi-walled CNTs

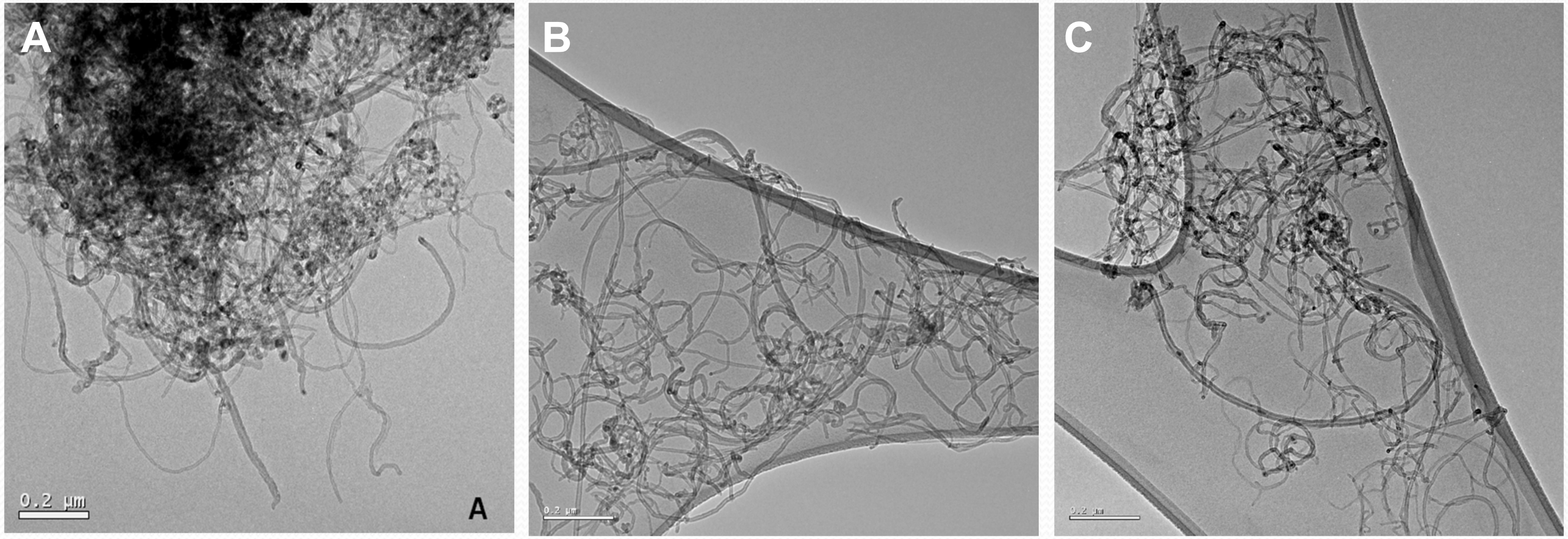
-- Fabricated by CVD (Iljin Nanotech)

-- Diameter: 10–20 nm

-- Length: 10–50 μm

TEM
-- CNT Dispersion

- **Dispersion states in ethanol**

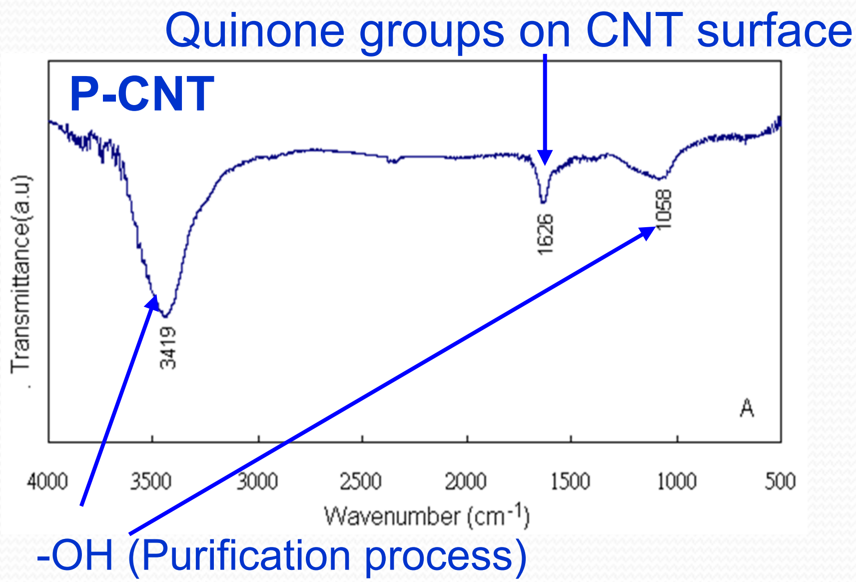


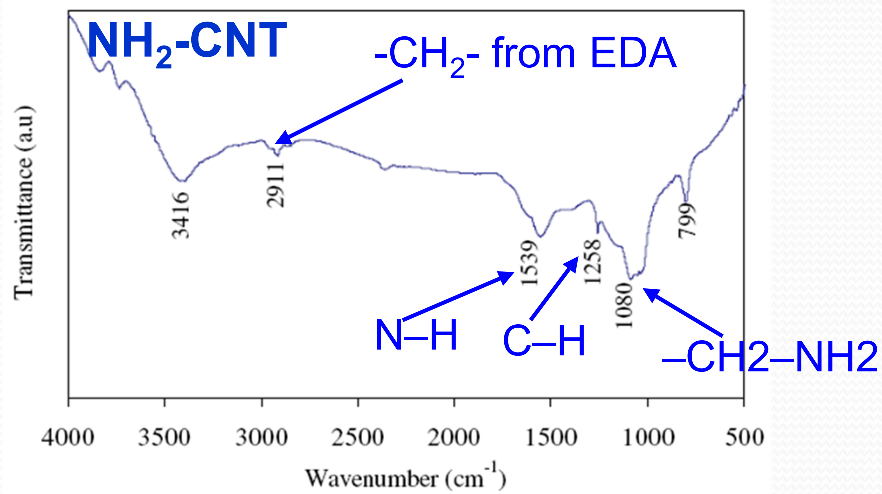
* Scale bar=0.2 um

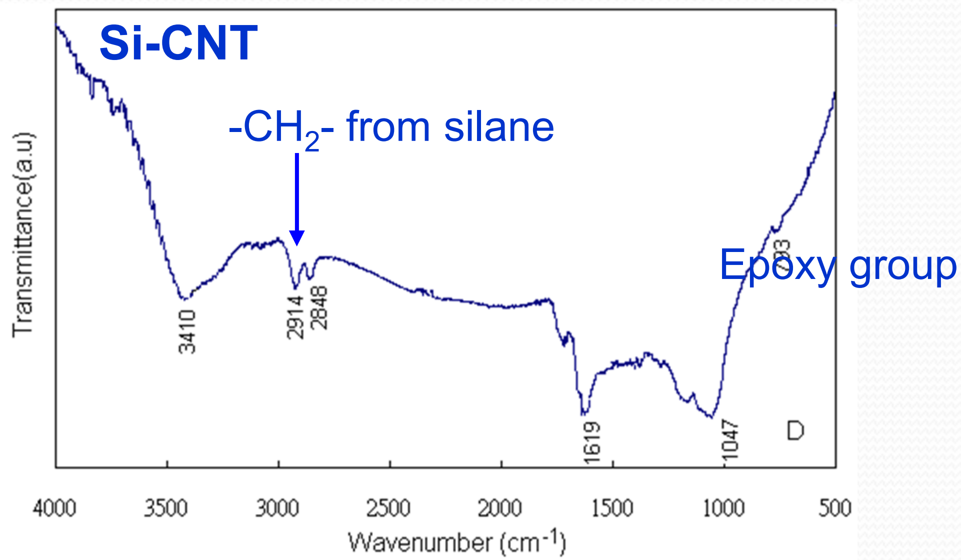
- A: P-CNT: Severe agglomeration, poor dispersion
- B: NH_2-CNT: Detached loosely with fewer agglomerates
- C: Si-CNT: Similar to B, without significant CNT agglomeration

FT-IR

-- Surface Functionalities of CNTs

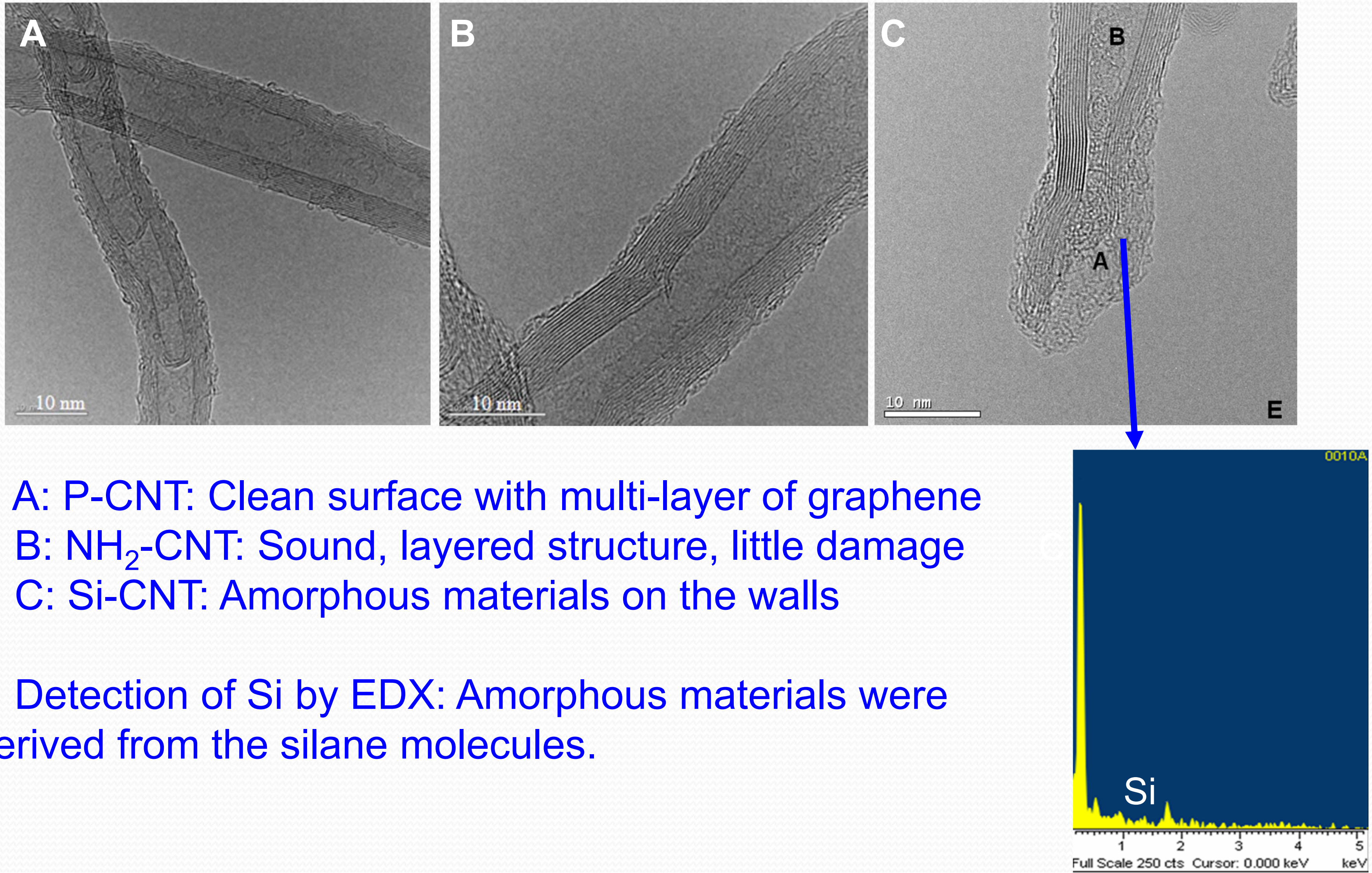






TEM and EDX
-- Evidence of Functionalities on CNT

- HR-TEM



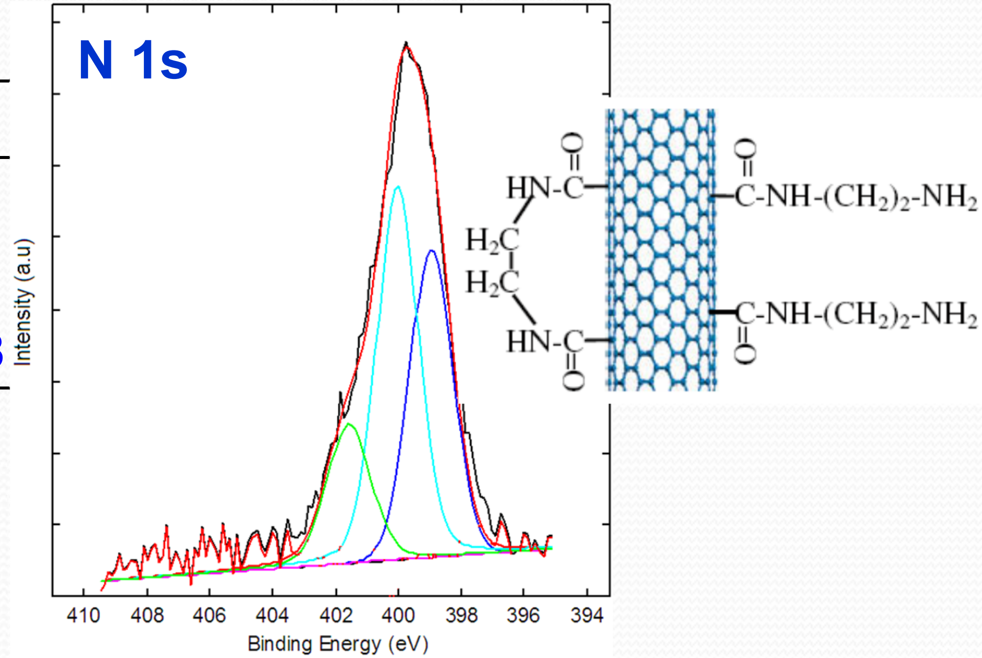
- A: P-CNT: Clean surface with multi-layer of graphene
- B: NH_2-CNT: Sound, layered structure, little damage
- C: Si-CNT: Amorphous materials on the walls

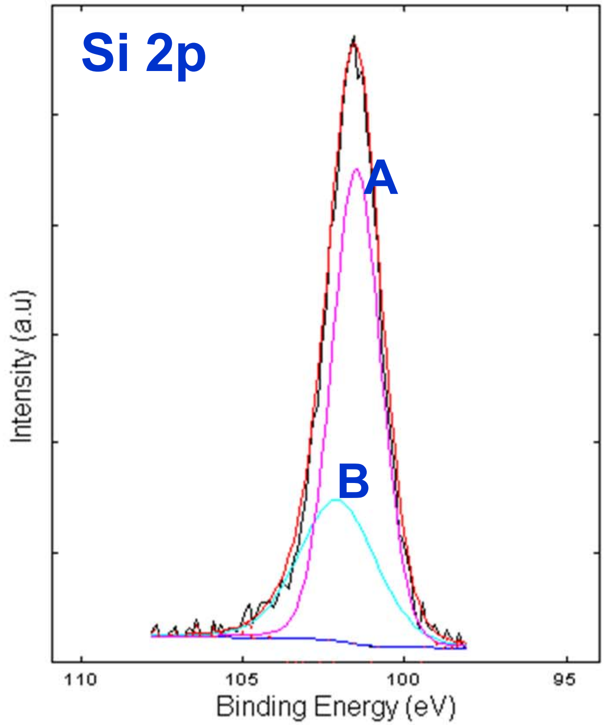
- Detection of Si by EDX: Amorphous materials were derived from the silane molecules.

XPS -- Reaction Mechanism

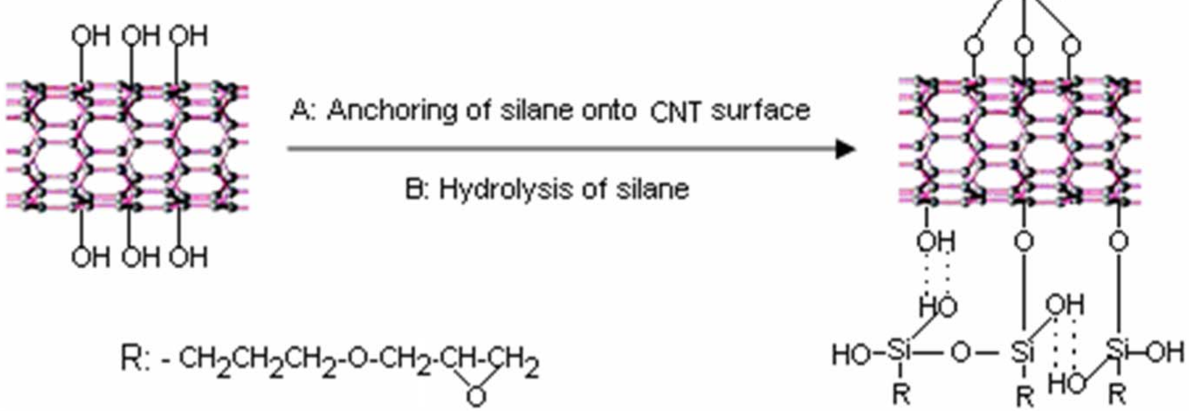
➢ Elemental compositions of CNTs

Element (at %)	C	O	**N**	**Si**
P-CNT	98.34	1.35	/	/
NH2-CNT	90.83	6.64	**2.53**	/
Silanized	88.51	9.38	/	**1.68**



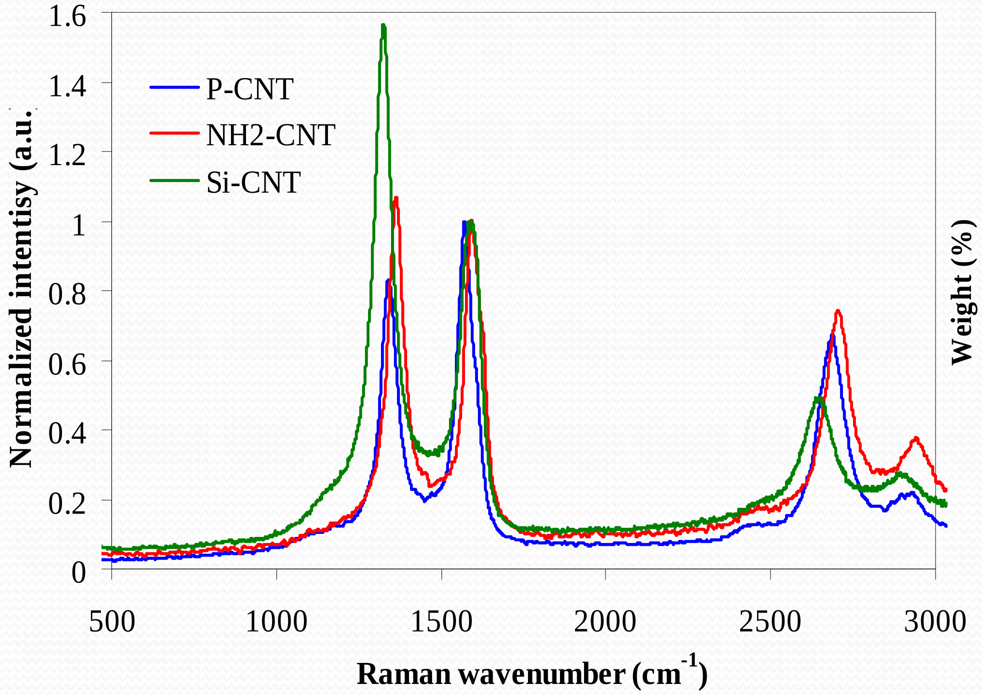


Peak contribution A:B= 80.03%:19.97%

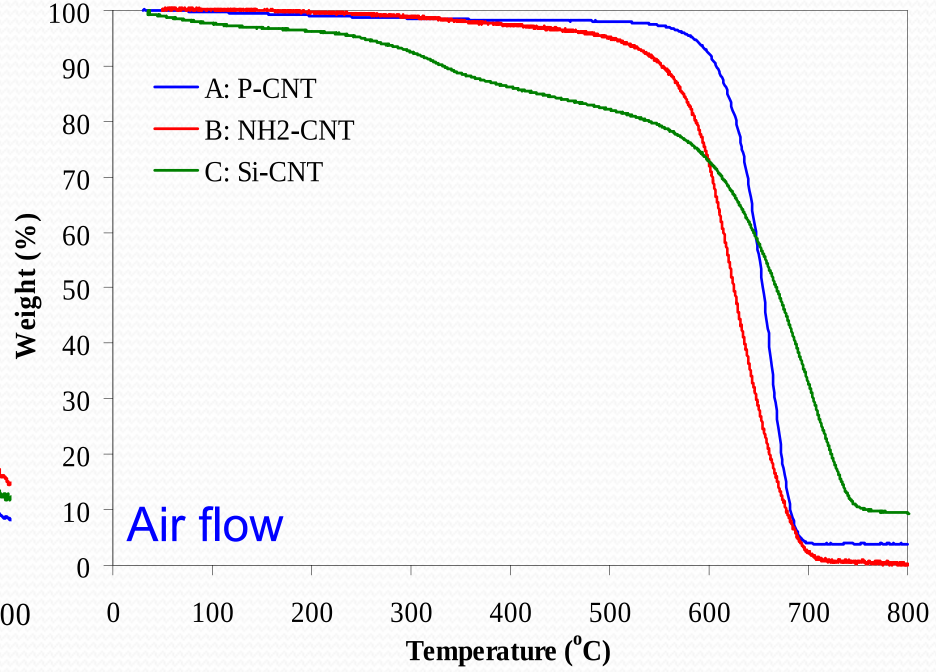


Degree of CNT Functionalization

Raman



TGA



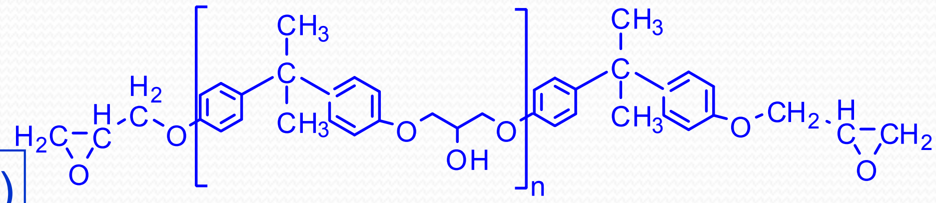
	D	G	G'	I_D/I_G
P-CNT:	1336.8	1568.4	2673.6	**0.82**
NH_2-CNT:	1360.1	1590.3	2700.1	**1.12**
Si-CNT:	1320.7	1580.7	2642.5	**1.58**

- **P-CNT:** 3% weight loss at 570 ^{o}C
- **NH2-CNT:** 14% weight loss at 570 ^{o}C
- **Si-CNT:** 22.6% weight loss at 570 ^{o}C

- **Higher I_D/I_G ratio** of Si-CNT: a higher degree of functionalization
- **Significant Raman shifts**: attachment of functional groups, charge transfer

Effects of Functionalization on the Properties of CNT/Epoxy Nanocomposites

➢ Nanocomposite Fabrication



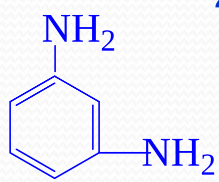
Epoxy (DGEBA)

↓ Degassing at 80 ℃ for 2h

CNT → Disperse in ethanol → Sonicated mixture → 1. Ultrasonic at 60℃ for 1h; 2. Ultrasonic at 80 ℃ for 1h

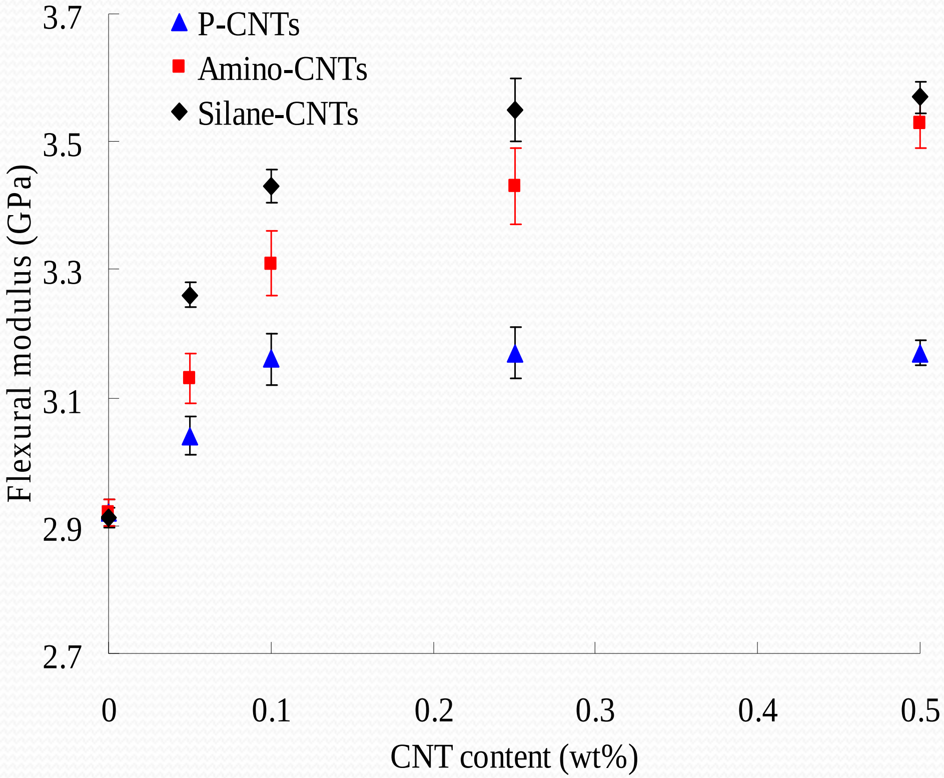
→ Vacuum oven at 80℃ for 5h →

↑ Curing agent (m-PDA) (14.5 wt% of epoxy)

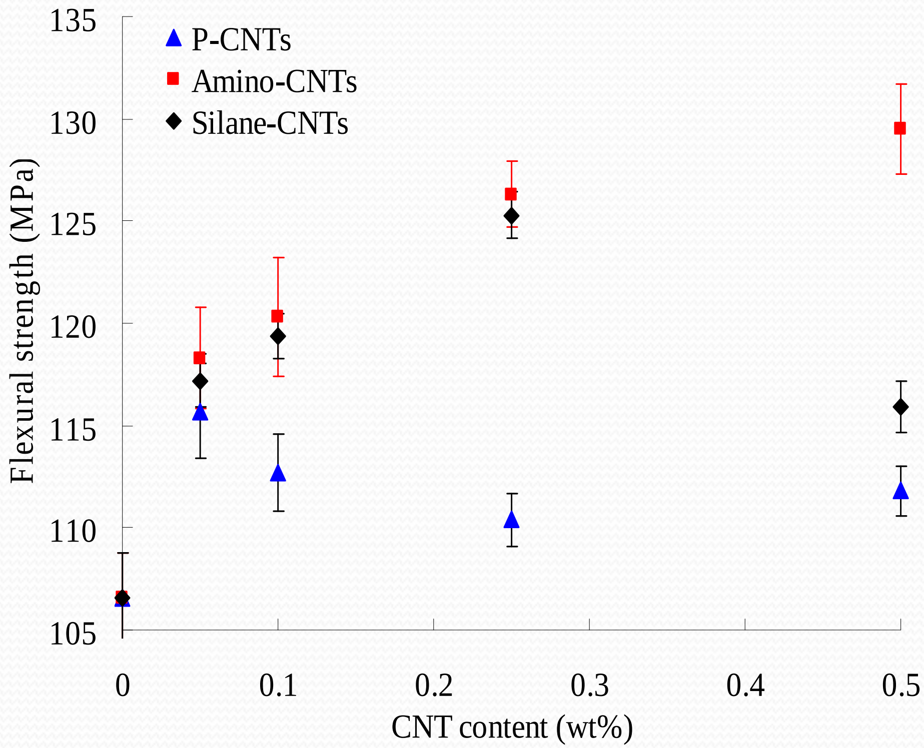


→ 1. Curing at 80℃ for 2h; 2. Curing at 150 ℃ for 2h → Nanocomposites

Mechanical Properties
-- Flexural Modulus and Strength



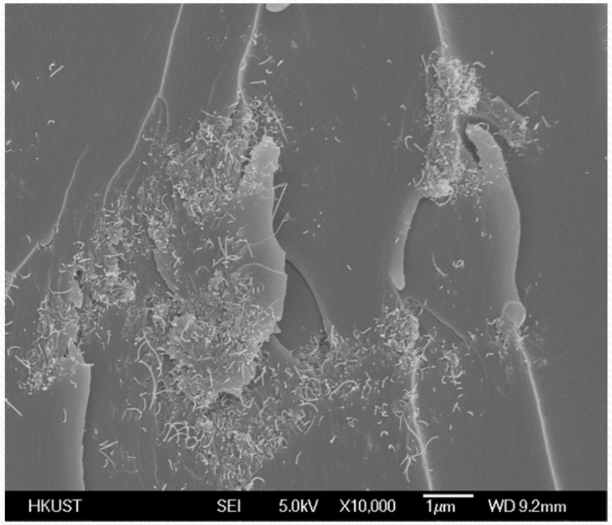
Flexural modulus



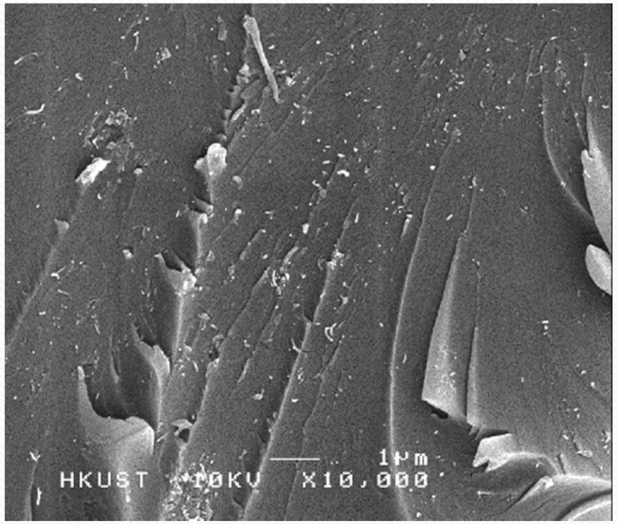
Flexural strength

- **Nanocomposites with functionalized CNTs**: A higher modulus and strength than the untreated-CNT counterparts
- **Anomaly in flexural strength when CNT= 0.5wt%,** curing reaction was affected by the silane-CNT due to higher degree of functionalization

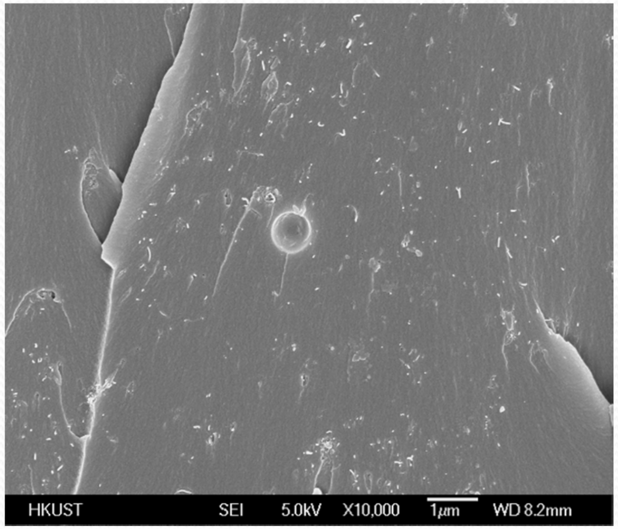
SEM
-- Dispersion of CNT in Matrix



0.25% P-CNT



0.25% NH2-CNT



0.25% Si-CNT

- **P-CNT**: mainly in the form of agglomerates, CNT pull-out
- **NH2-CNT**: Much enhanced dispersion without agglomeration
- **Si-CNT**: Uniform dispersion

Mechanism behind the Enhancement on Mechanical Properties

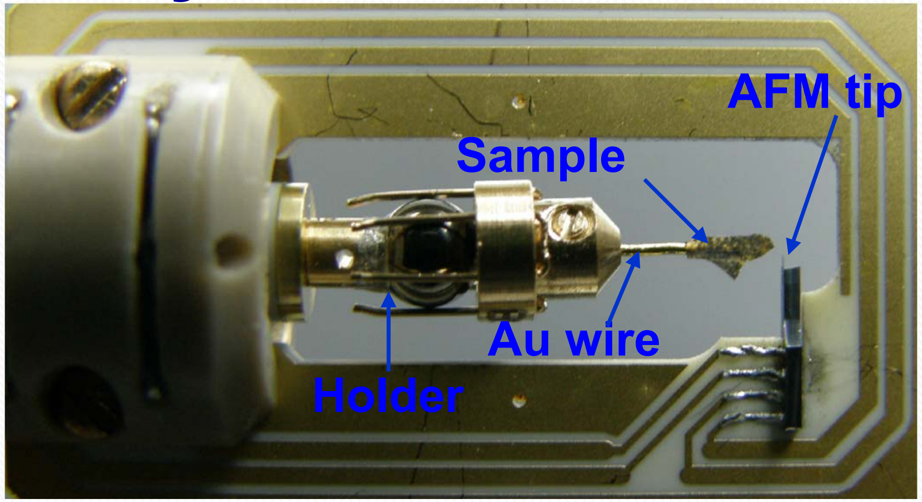
- **Macroscale vs. Microscale**

- **Characterization on the Interactions between CNTs and Polymer Matrix**

  -- Fibre pull-out (Direct method)

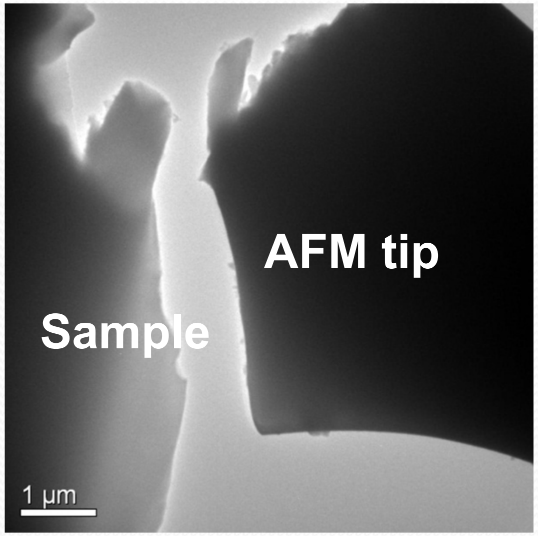
  -- Raman spectrometry (Indirect method)

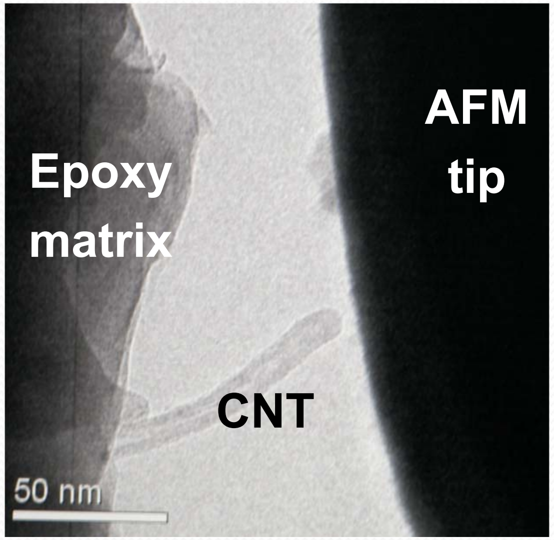
Fibre (CNT) Pull-out from Matrix
-- Interfacial Strength between CNT and Polymer Matrix



➤ **Sample preparation**

-- Pristine CNT/epoxy composites
-- Polished sample with T ~0.1 mm
-- Fractured in liquid nitrogen to get sharp fracture surface



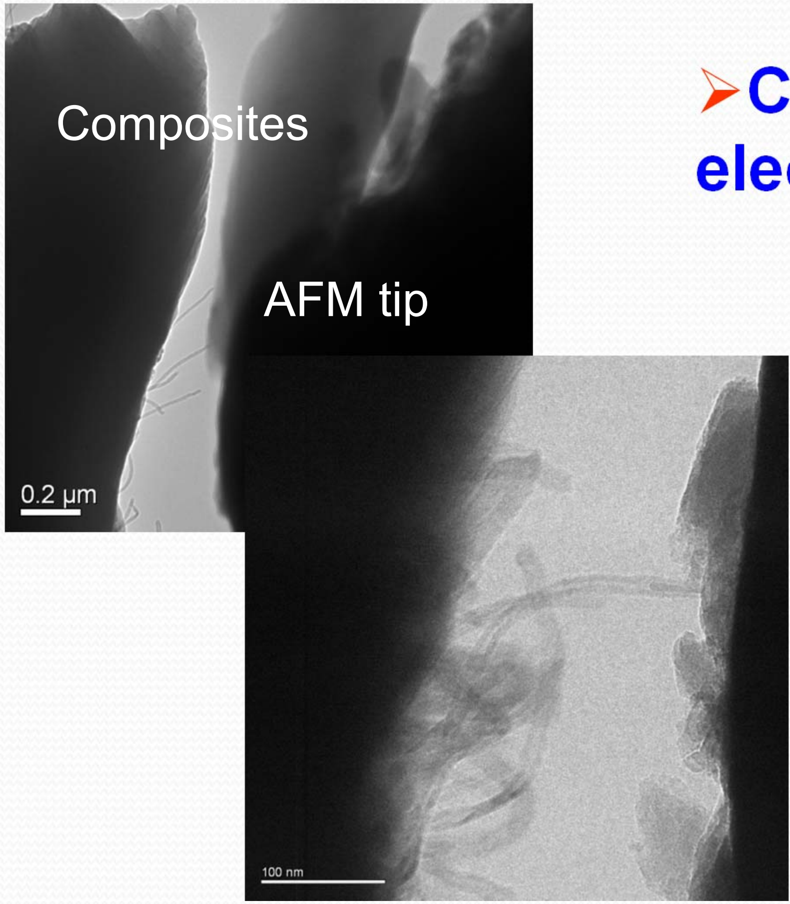


➤ **How to connect CNT with AFM tip?**

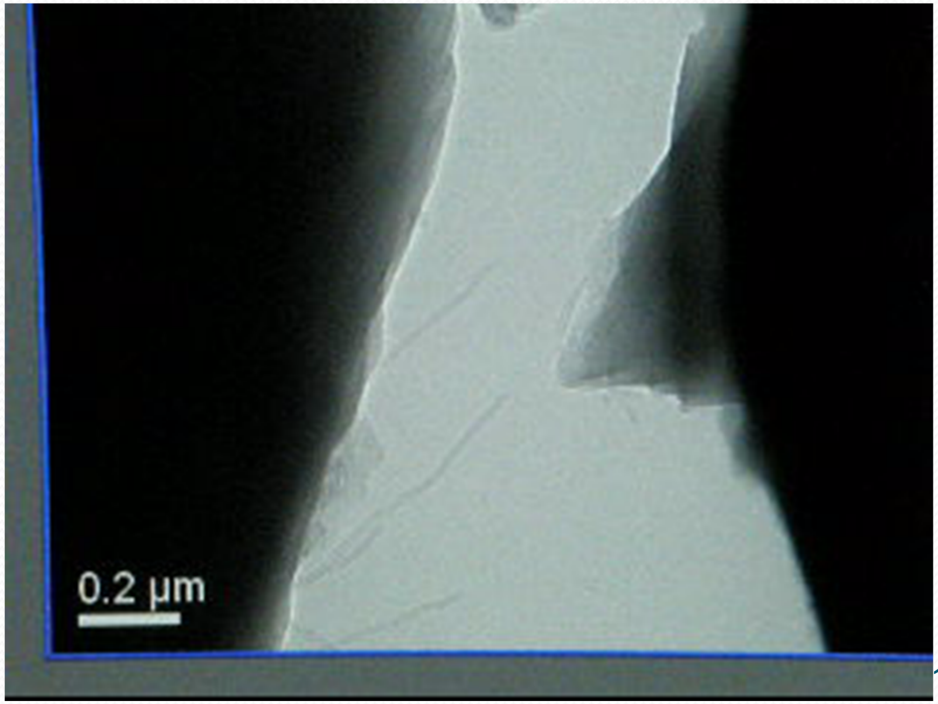
-- High content: CNT=0.5%;
-- Poor interaction between
-- CNT and AFM tip (made of Si compounds, sharp and clean surface)

Electrostatic Interaction between CNT and AFM Tip (I)

- **AFM tip:**
  - -- Deposition of contamination (Composites impacted the AFM tip)

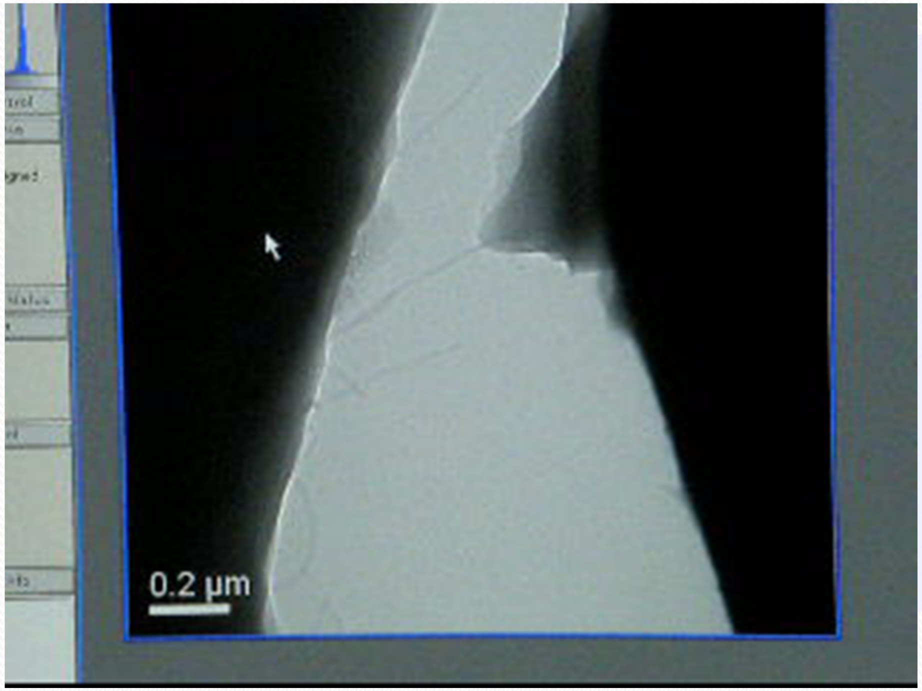


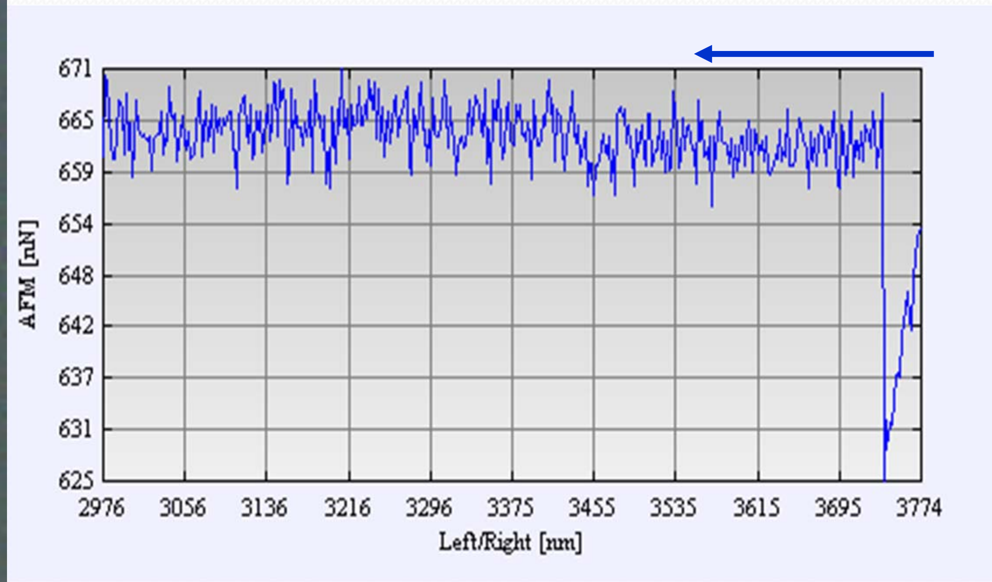
- **CNT connection with AFM tip via electrostatic interaction**



Electrostatic Interaction between CNT and AFM Tip (II)

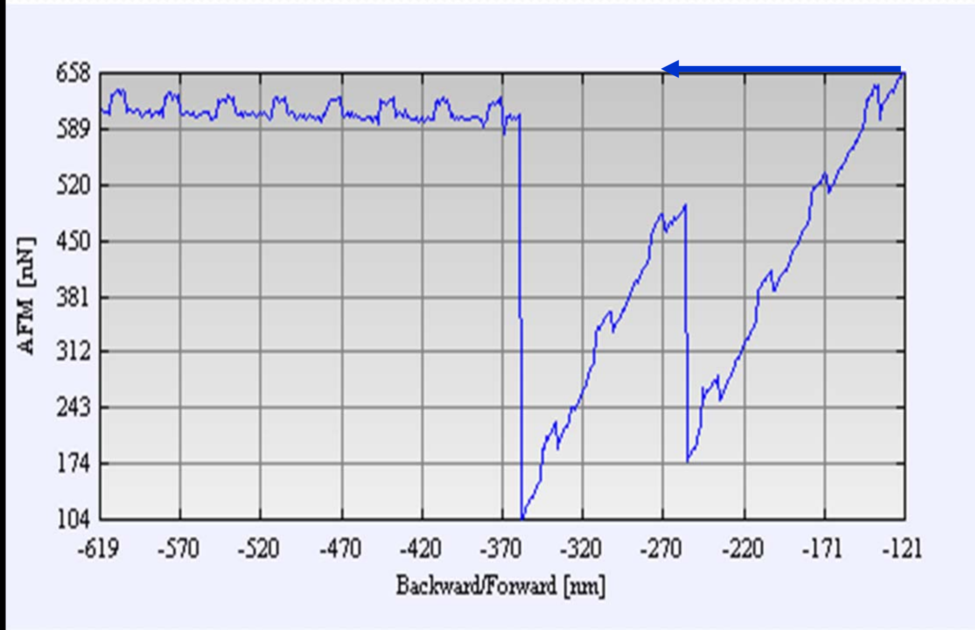
- Weak electrostatic interaction





Electrostatic force between CNT and composites is ~ 40 nN

Connection of CNT with AFM Tip by Electron Beam Bombardment

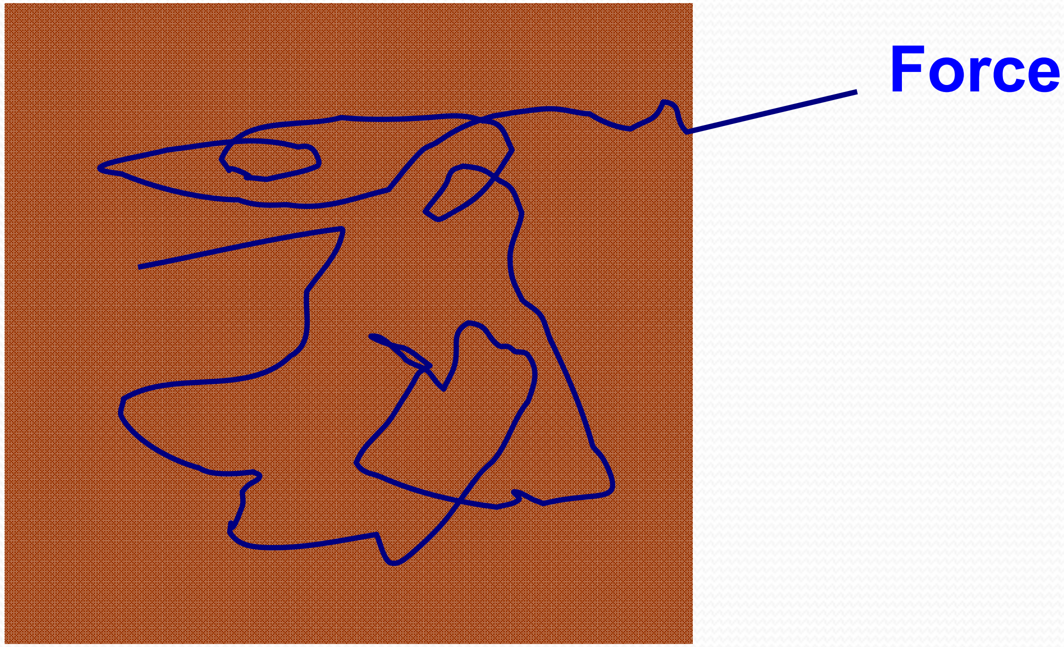


- Better bonding between CNT & AFM tip;
  -- Deformation (flexibility) of CNT;
  -- Pull-out of CNT from matrix from load-displacement curve.

- Estimated interfacial force between CNT and matrix: > 410 nN, at least 9 times higher than that of electrostatic force

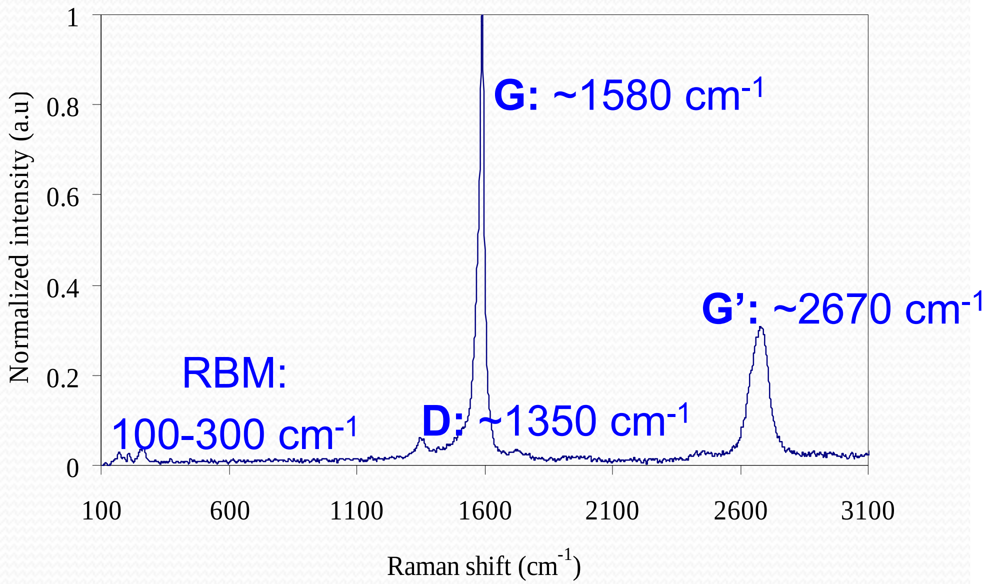
Difficulty/Bottleneck of Pull-out Experiment

- **Technique**
  - -- CNT bonding with AFM tip;
  - -- CNT connection with tip (3-D manipulation in 2-D view)
  - -- Matrix (Thermosetting polymer)
- **Theory**

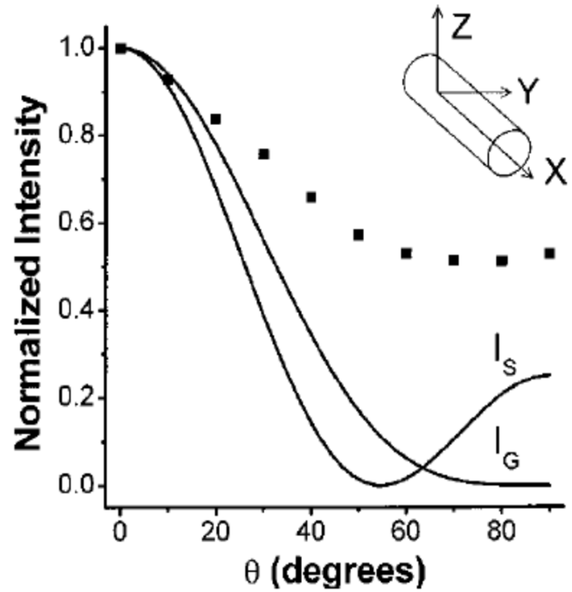


Roman Spectrometry vs. Load Transfer

- **Raman spectrometry of CNTs**



- **Random CNTs Vs Raman sensitivity**



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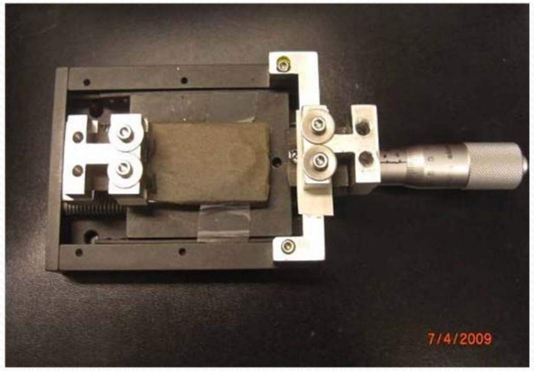
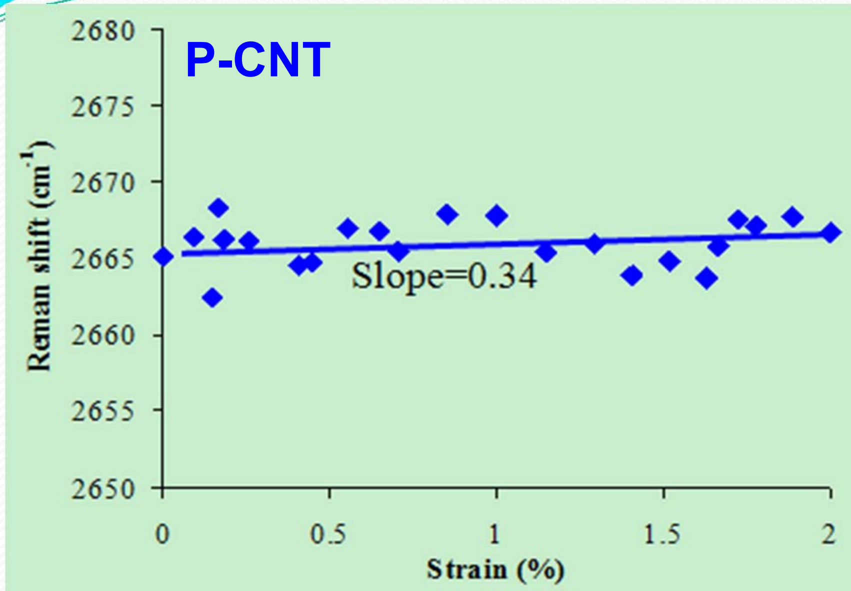
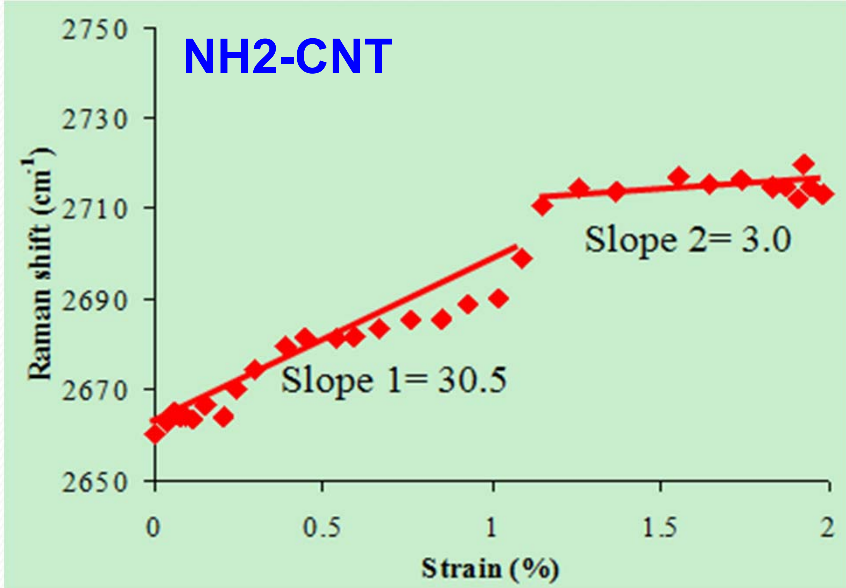
- **G' band**: Sensitive to any changes in the C-C bond vibrations
- **Using polarized light**, random distributed CNTs can be used as strain sensors
- **Experiment**

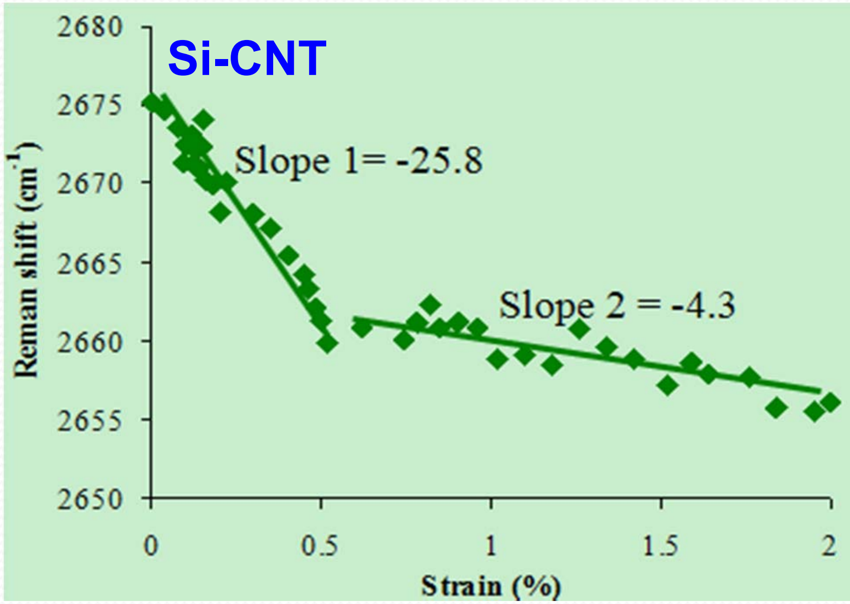


- RM3000 Micro-Raman:
- Laser: He-Ne, 632.8nm, 20 mW,
- Beam size: 2-3 um, 5% of full power, Objective: 50X

Behavior of Load Transfer from Matrix to CNTs







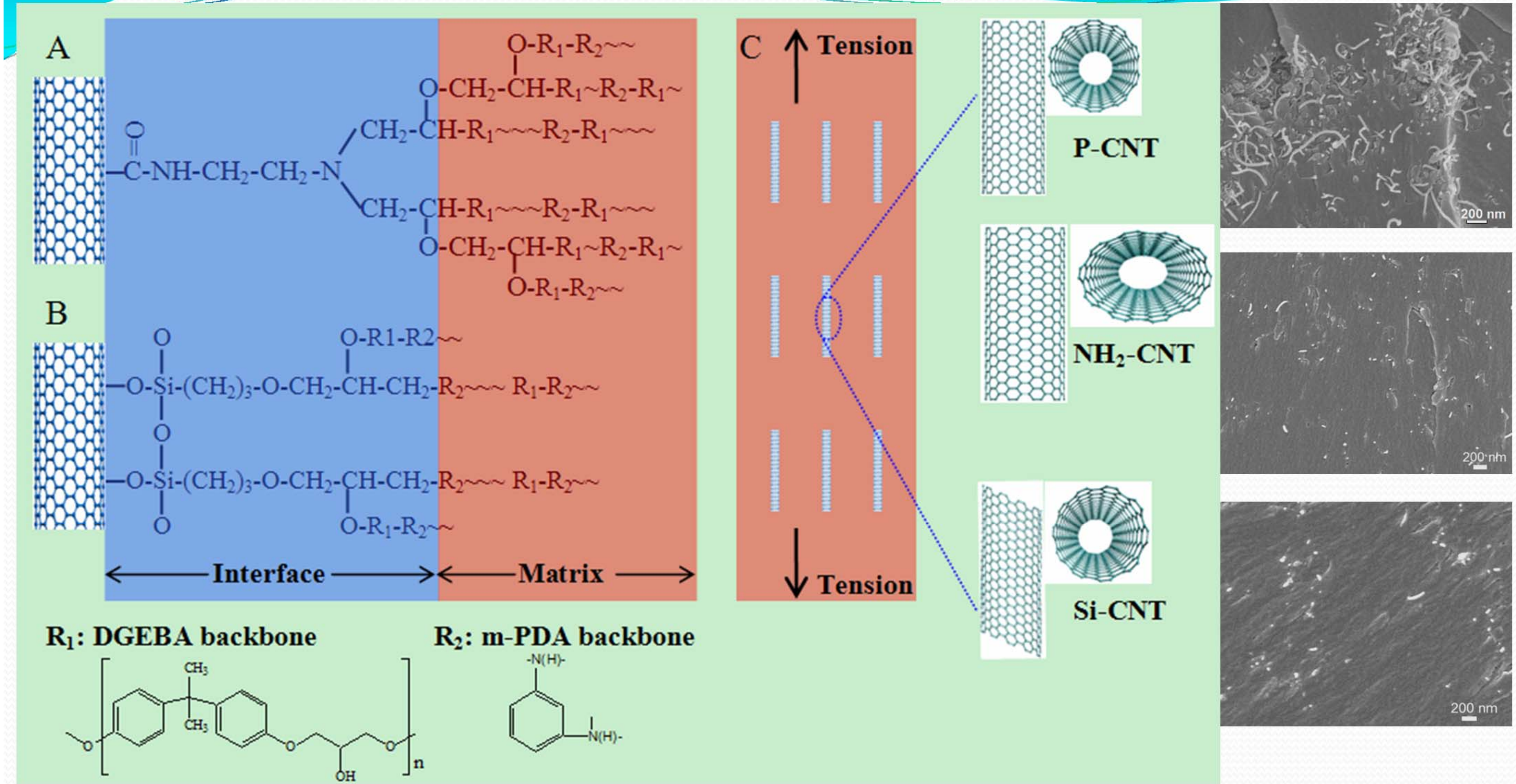
- **P-CNT**: Small change in G'-band, poor load transfer from matrix to CNTs
- **NH2-CNT**: Significant upshift
- **Si-CNT**: Significant downshift

- **Deformation of CNTs in Matrix:**

-- Compression mode (with "+ "slope)

-- Tension mode (with "-" slope)

Load Transfer and Interface

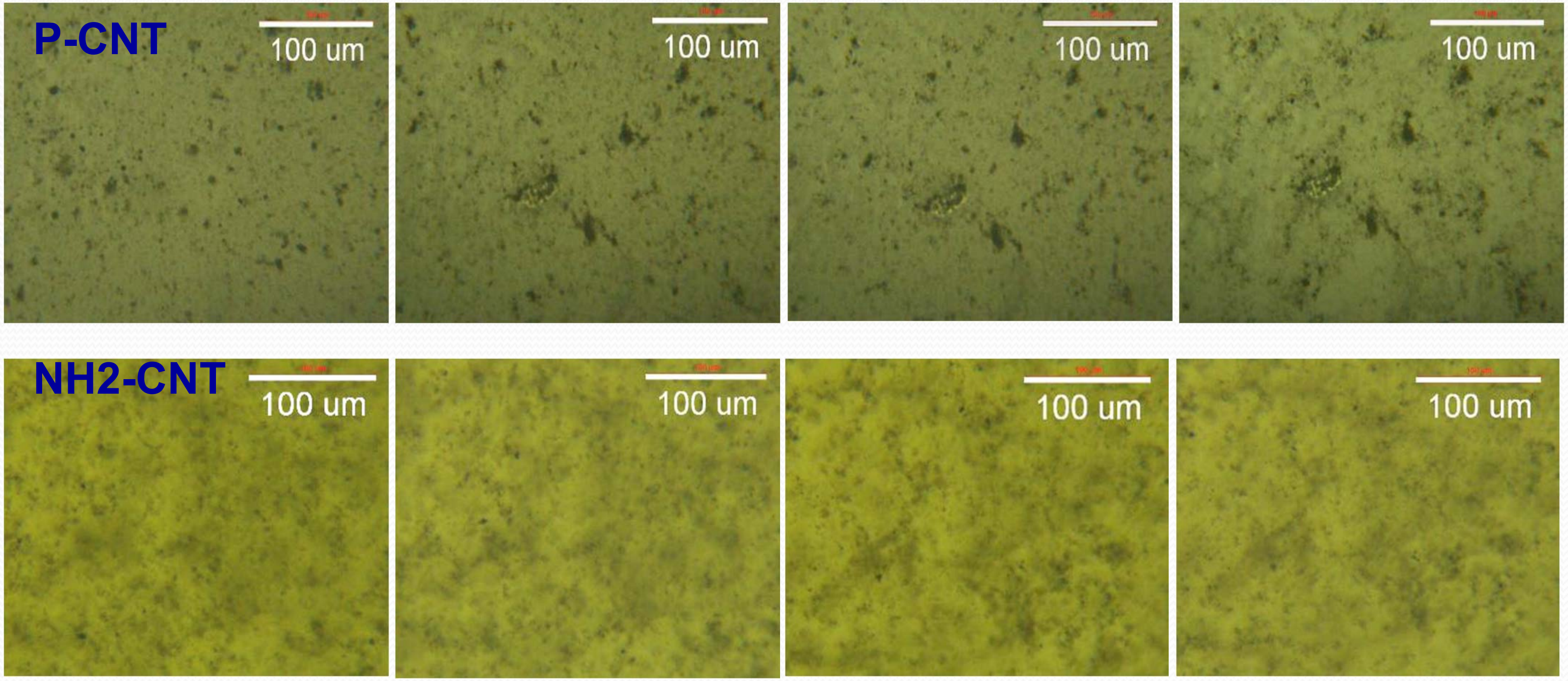


- **Structure of interface**
  - -- **NH2-CNT**: Similar to that of matrix
  - -- **Si-CNT**: -Si-O-Si- structure, similar to silicon rubber

Shear modulus: Epoxy ~ 1.0 GPa, silicon rubber ~ 10 MPa

Behavior of Dispersed CNTs in matrix

➢ **Transmission optical images of dispersed CNTs in epoxy matrix during curing**



Curing time 0 2 5 60 minutes

➢ **P-CNT**: Re-agglomeration at the initial stage of curing (1–5 min), more pronounced the matrix-rich regions (transparent regions) with increasing time of curing

➢ **NH2-CNT**: Fairly uniform and little changed regardless of curing time

Summary

- Attachment of functional groups onto CNT surface resulting in improved dispersion
- Improved mechanical properties of nanocomposites with functionalized CNTs
- Degree of CNT functionalization: Adverse effect for epoxy curing at a higher loading of CNTs
- Load transfer: Dominated by the nature of functionalities on CNTs and resulted CNT/polymer interface
- Functional groups on CNTs effectively inhibit the re-agglomeration of CNTs during the curing of resin

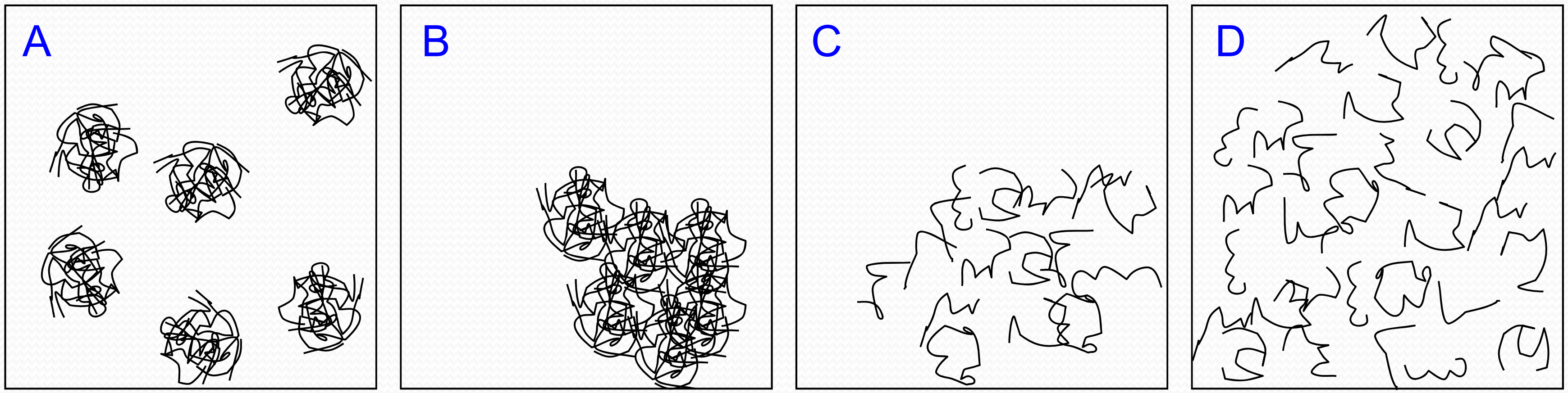
Fundamental issues of CNT/polymer nanocomposites

Dispersion of CNTs

- Characterization of CNT dispersion
- Correlation between CNT functionalization & dispersion

Fundamental Questions on CNT Dispersion

- Why and how to evaluate CNT dispersion?
- Is “average agglomerate size” a quantitative measure of dispersion?
- Are the dispersion states really different at different magnifications: nano-, micro- and macro-scale?
- How dispersion correlate with processability and various properties of composites?
- Are there correlations between functionalization and dispersion?
- **Dispersion Vs Distribution**



A: Good distribution but poor dispersion; B: Poor distribution and poor dispersion; C: Poor distribution but good dispersion; D: Good distribution and good dispersion.

Objectives and Methodology

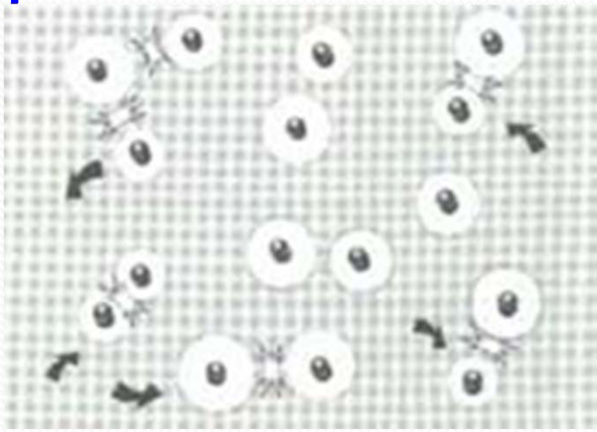
➢ **Objectives**

-- To evaluate CNT dispersion

-- To establish correlation between surface properties obtained from different techniques (XPS, Goniometry, **zeta-potential)**

-- Variables: different CNTs and CNT functionalization

➢ **Quantitative evaluation of CNT suspension stability using Zeta potential**



➢ **Zeta potential (Electrokinetic potential in colloidal systems)**

-- The potential difference between the **dispersion medium** and the **stationary layer of fluid** attached to the dispersed particles

➢ **Behavior of particles in a solution**

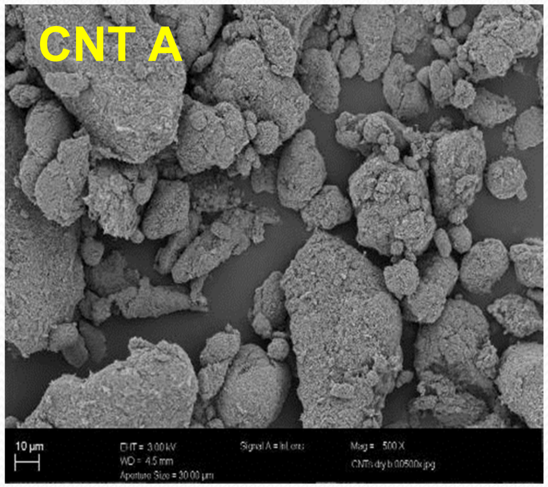
-- Dispersed particles are electrically charged due to their **ionic characteristics** and **dipolar attributes;**

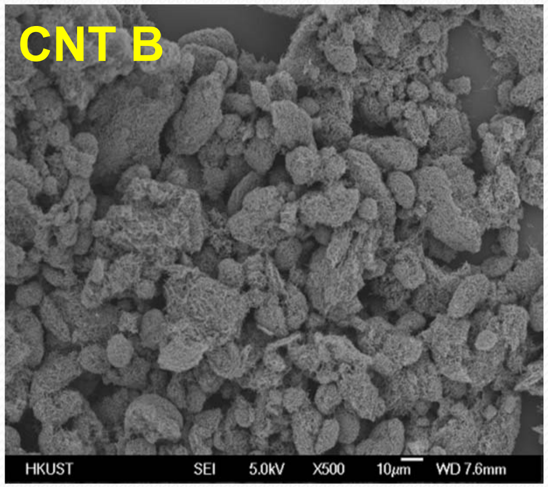
-- Each particle dispersed in a solution is surrounded by **oppositely charged ions**. This area is called the **diffused double layer**

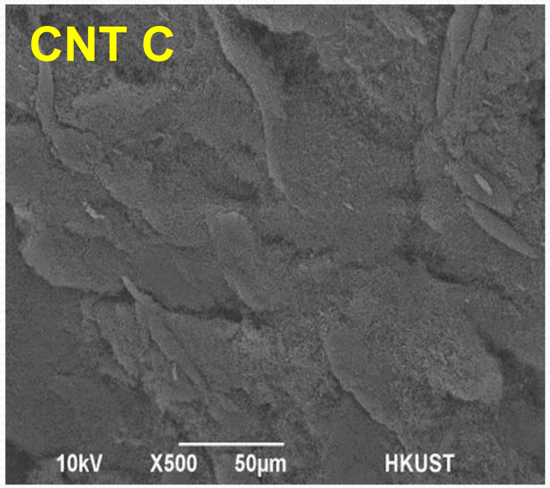
CNTs with Different Properties

CNTs	Dimension	Supplier	Remarks
CNT A	MWCNTs with diameter 10-20 nm and length 20-50 μm	Iljin	As produced
CNT B	MWCNTs with diameter 40-60 nm and length 10-40 μm	NanoKarbon	Ethanol treated
CNT C	MWCNTs with diameter 40-60 nm and length 10-40 μm	NanoKarbon	As produced

➢ **SEM images of CNTs at dry states**



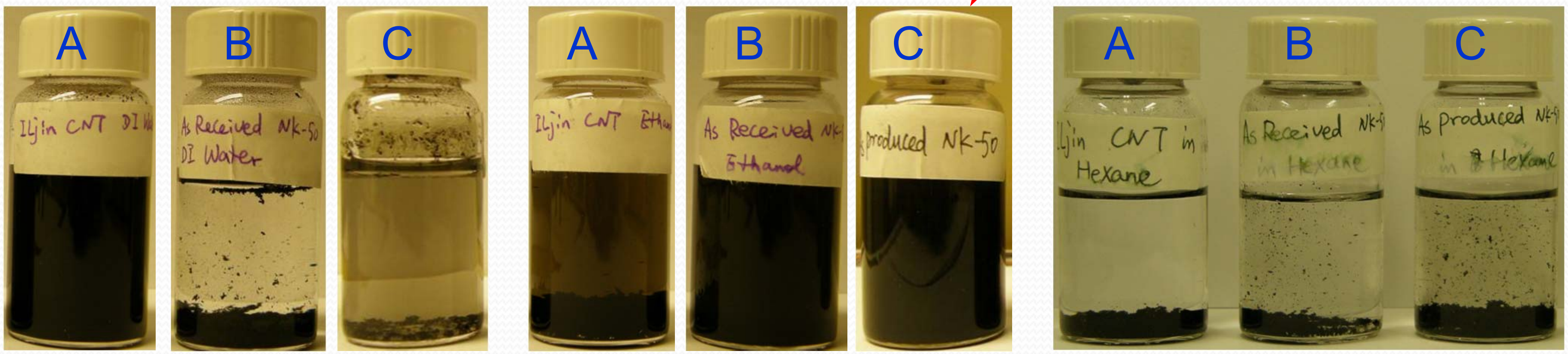




Zeta potentials of CNTs (I)

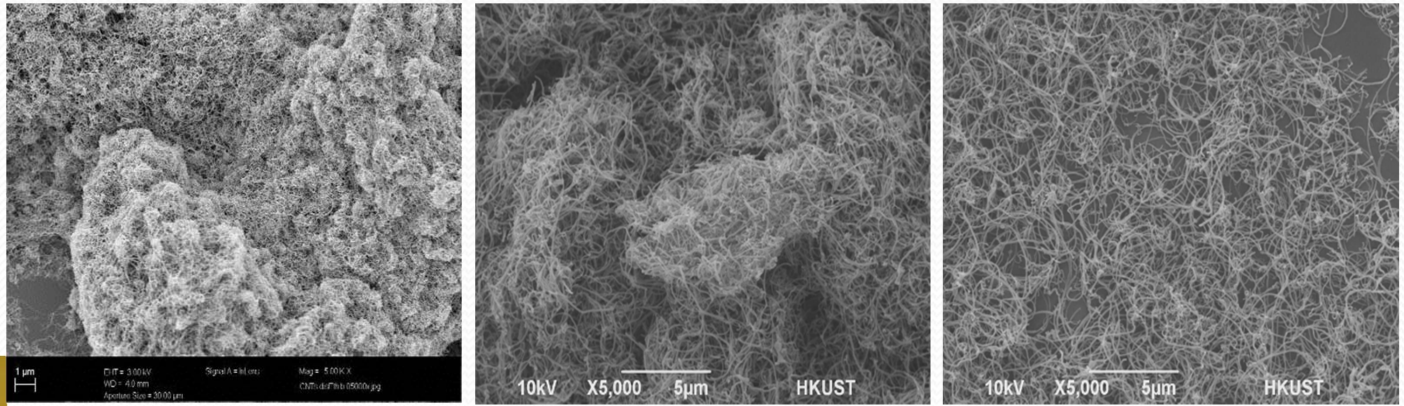
CNT / Solvent	(A) (mV)	(B) (mV)	(C) (mV)
Water	**-24.8 ± 2.2**	+10.3 ± 1.4	+19.8 ± 1.8
Ethanol	-18.0 ± 3.5	**-26.3 ± 10.8**	**-44.4 ± 7.0**
Hexane	-10.4 ± 5.4	+6.18 ± 2.0	+19.3 ± 3.2

Water　　　　Ethanol　　　　Hexane



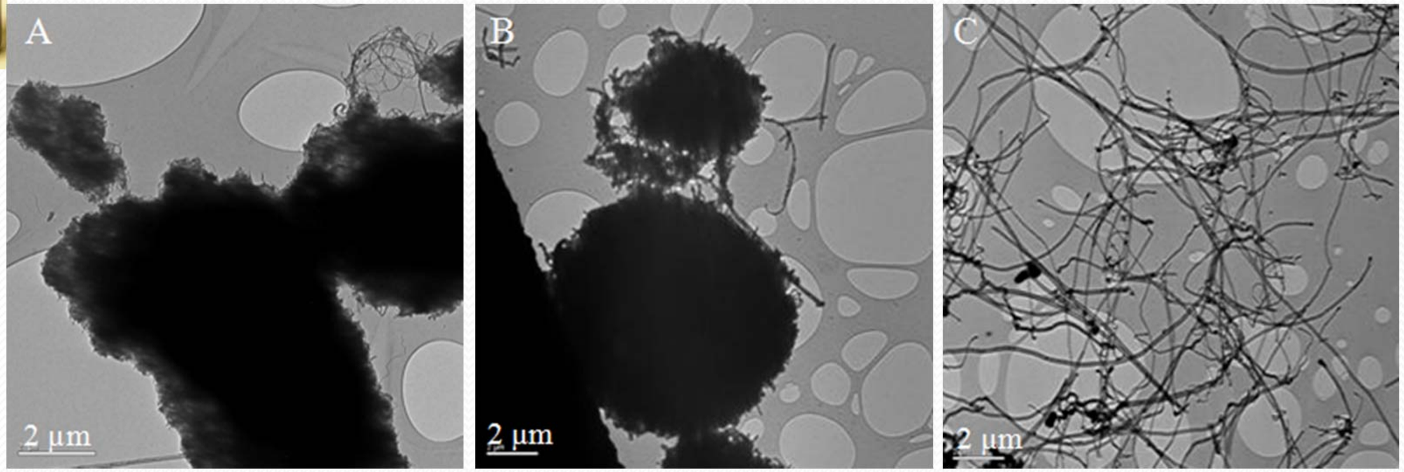
- Good correlation between Zeta potential and suspension stability of CNT colloids

Zeta potentials of CNTs (II)



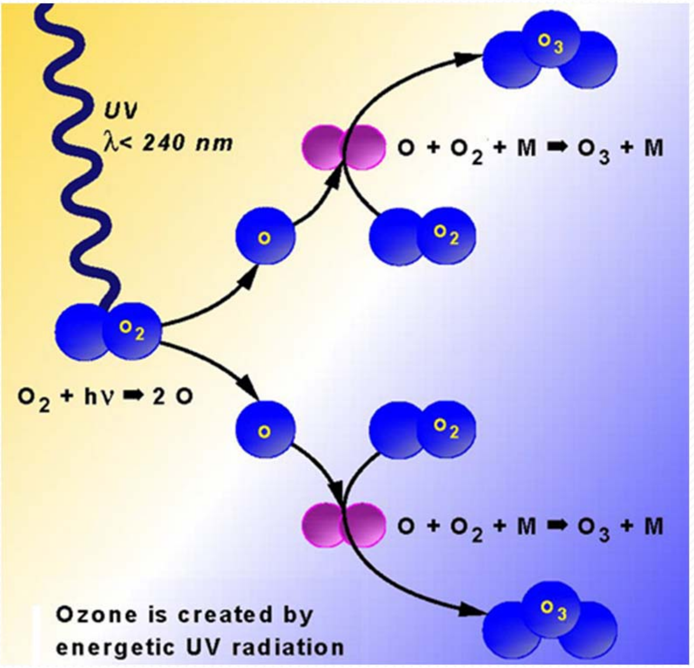
- **Zeta potential and dispersion**
  - **~ 25 mV**: Related to the micro- & macroscopic dispersion
  - **> 40 mV**: An indication of high quality CNT dispersion

CNTs in ethanol



Correlation between CNT Functionalization and Dispersion

- **CNT functionalization**

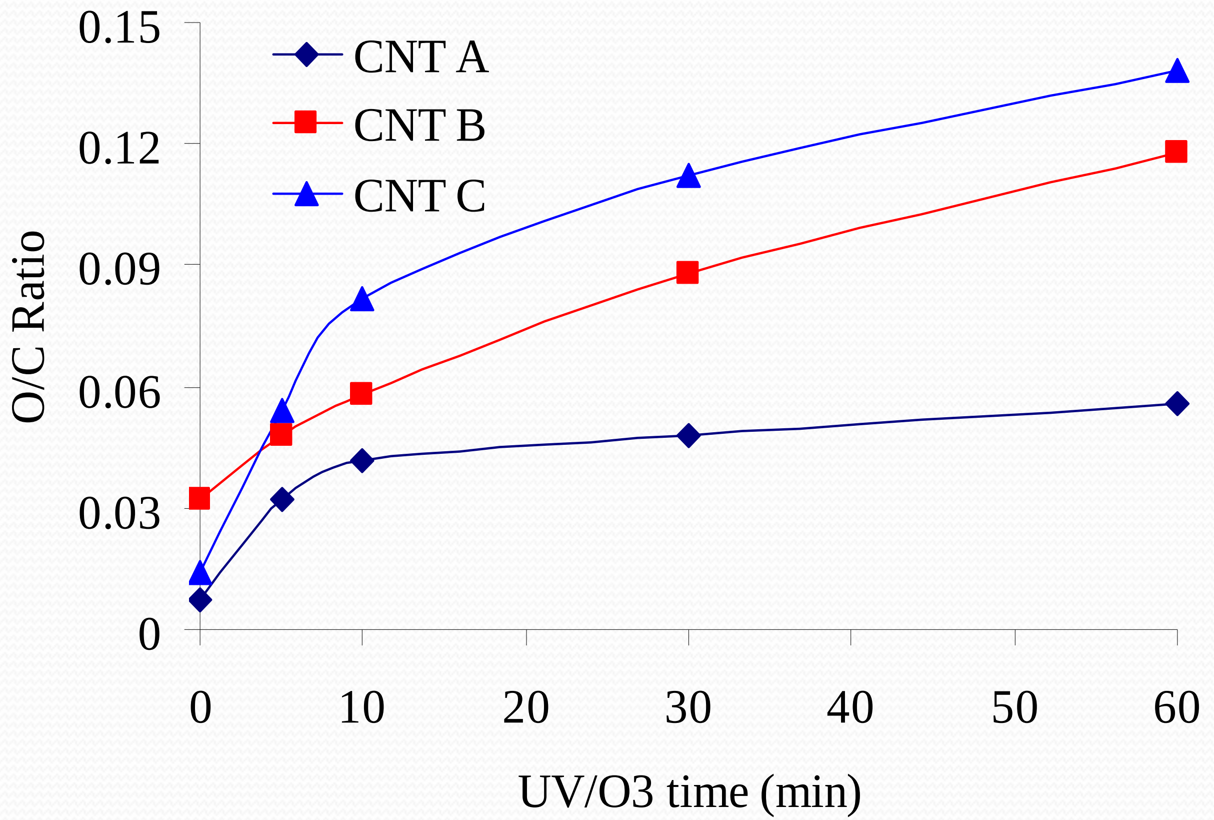


UV/O_3 treatment for different durations

- **Reactions of Ozone under UV**

O_3 + *hv* (253.7nm) → $O^{atm} + O_2$
$O^{atm} + O_2 \rightarrow O^G + O_2$
$O^{atm} + O_3 \rightarrow O_2 + 2O^G$
$H_2O + O^{atm} \rightarrow 2\ {\cdot}OH$

XPS of Different CNTs



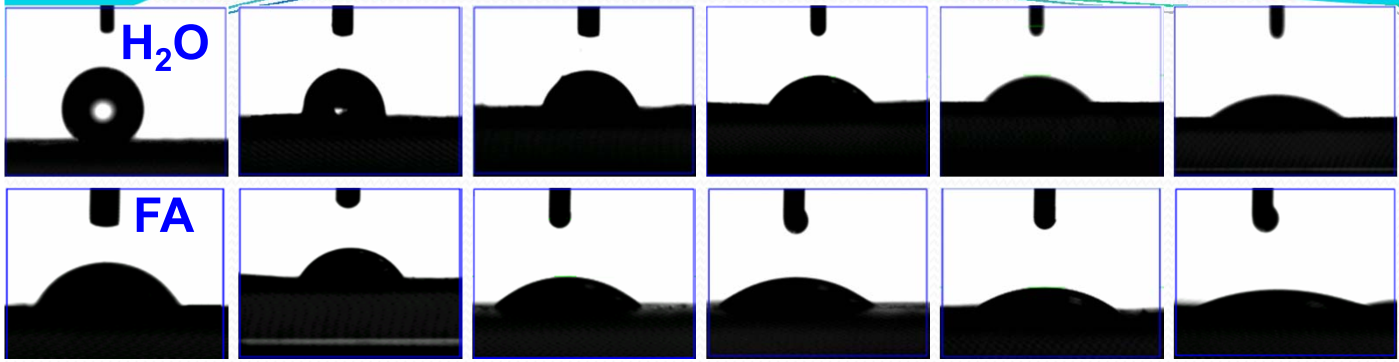
- **CNT C**

  -- Lower oxygen content than CNT B before treatment

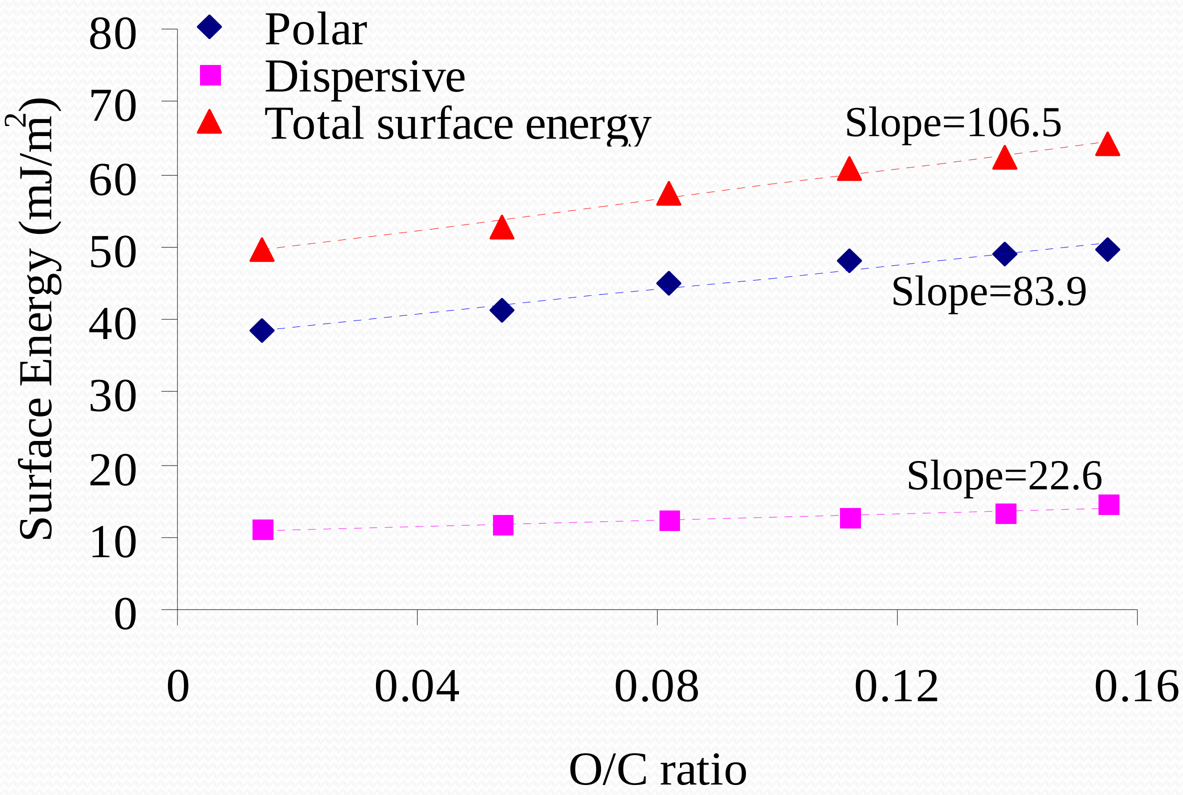
  -- Easier to attach oxygen (easier functionalization due to better dispersion)

  -- Estimated ~ 5 min UV/O_3 would produce the same oxygen content of neat CNT B (before treatment)

Surface Energy of CNTs

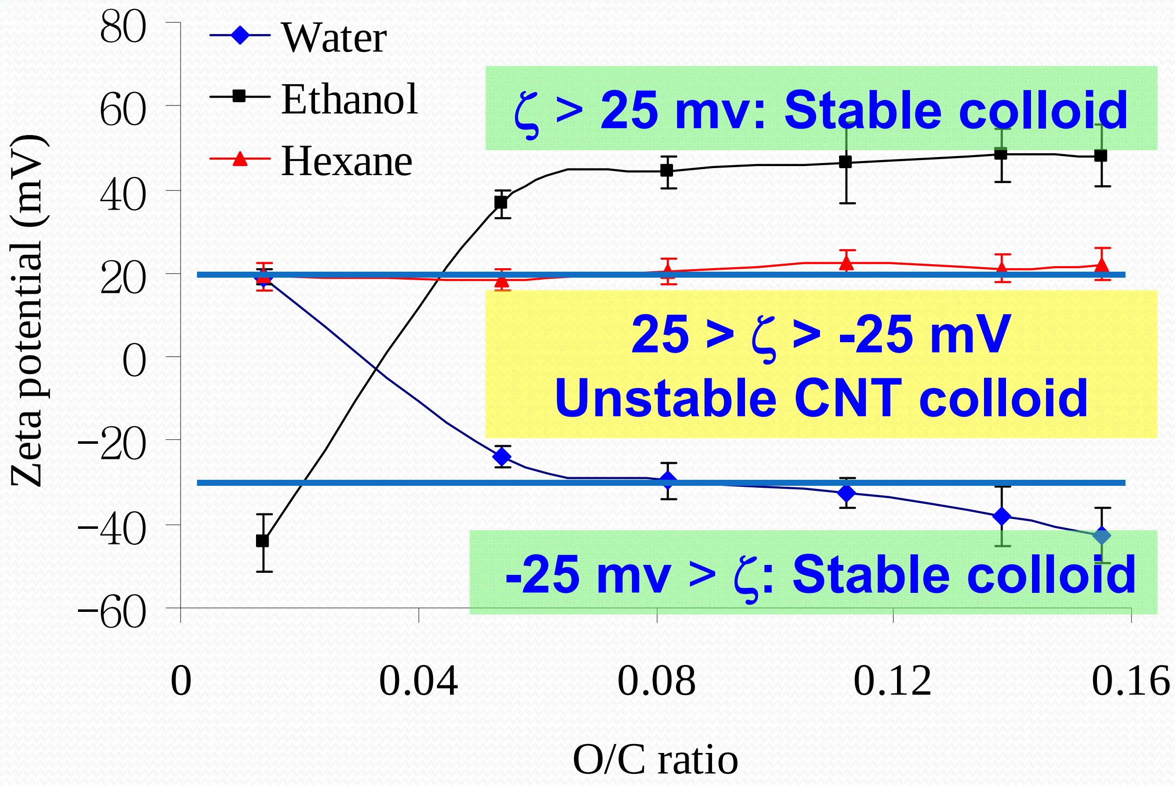


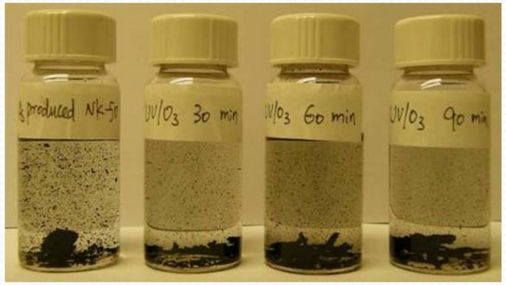
- Significant decrease in contact angle after UV/O_3 treatment: Transition from ***Hydrophobic*** to ***hydrophilic*** surface



- Linear increase in surface energy (contact angle) with O/C ratio (XPS)
- Two effects of UV/O_3:
  -- Polar (Functional groups): more pronounced effects
  -- Dispersive (non-polar)
- Correlation between **wettability and surface chemistry**

Zeta Potentials of Functionalized CNTs





Before sonication

24 h after sonication

CNT-C in **ethanol** for 30 S; C_{CNT} = 0.2 mg/mL.

- **Water: Polar solvent**; potential **"+" → "-"**; the longer the UV/O3 exposure, the higher the zeta potential.
- **Ethanol**: **Highly polar solvent**; potential **"-" → "+"**; Saturation of potential after 10 min exposure to UV/O3
- **Hexane**: **Non-polar solvent**; Little change in potential after UV/O3 exposure; Poor suspension stability

Summary

- Absolute value of zeta potential: Indication of CNT dispersion quality

  -- ~ 25 mV: Micro- and macroscopic dispersion

  -- > 40 mV: High quality CNT dispersion with enhanced suspension stability
- The higher degree of CNT functionality, the higher of absolute zeta potential value, most pronounced in a hydrophilic liquid such as water
- A linear correlation between the surface energy of a CNT film and the O/C ratio of CNT
- **Governing factors** for CNT dispersibility in a liquid:

  -- Physical states (entanglements and disentanglement)

  -- Hydrophilicity and surface functionality of CNTs

  -- Polarity of solvents

All of which are reflected by zeta potential

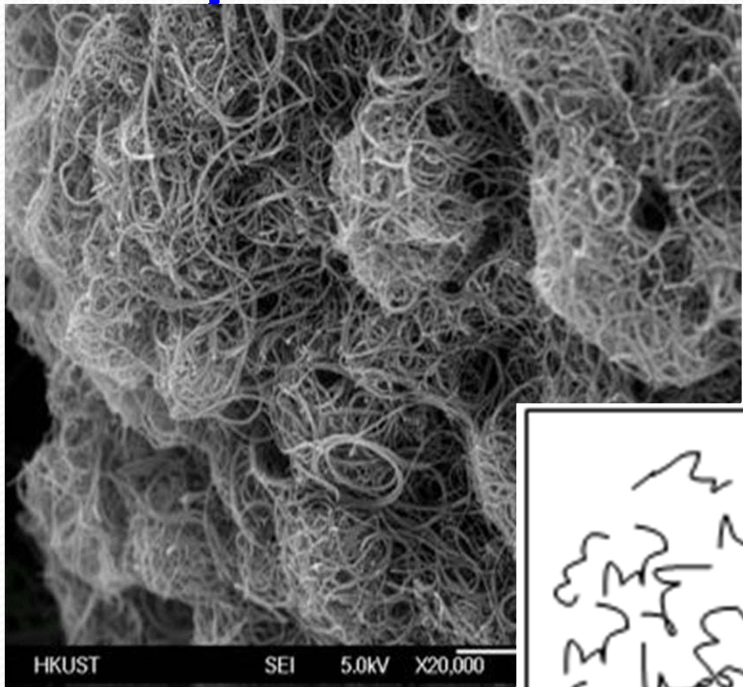
Fundamental issues of CNT/polymer nanocomposites

Nanocomposites Reinforced by Carbon Nanotube Foams

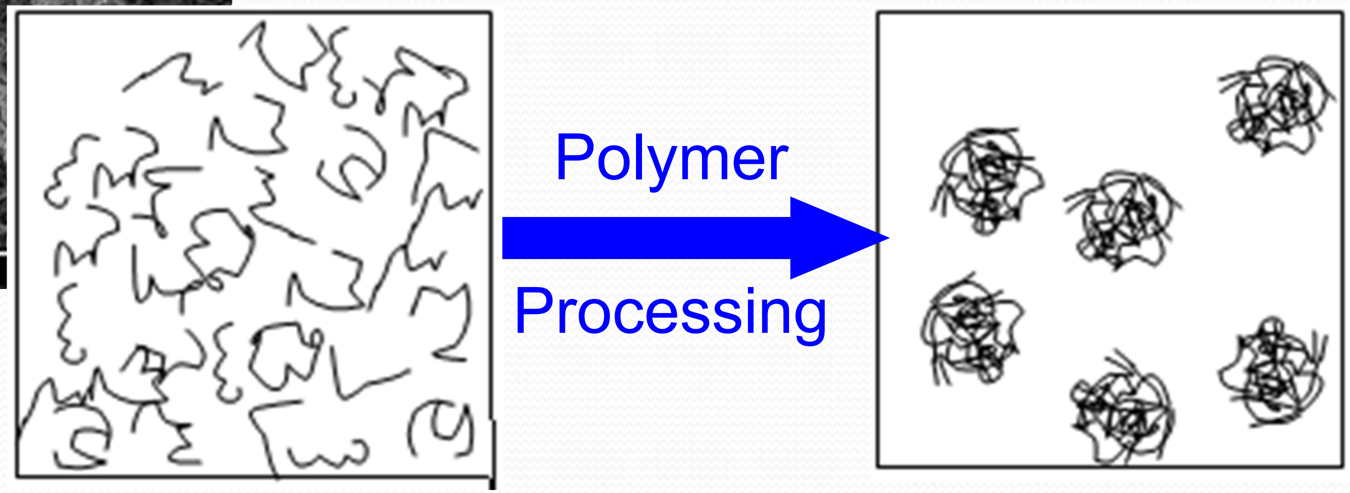
- Why CNT Foam?
- Preparation of CNT Foam
- Mechanism on the formation of foam
- Properties and application of CNT foam

Problems in Preparing CNT/Polymer Nanocomposites

- **Dispersion Issues**

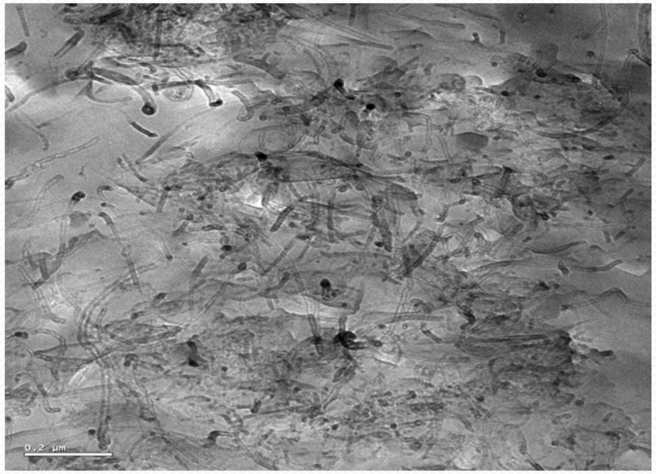


- **Re-agglomeration issues**

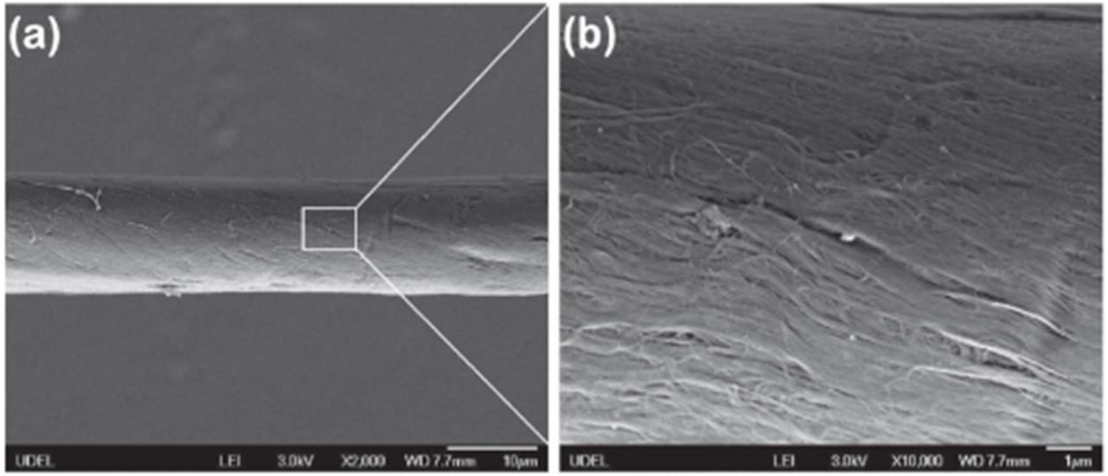


How to Solve the Problems?

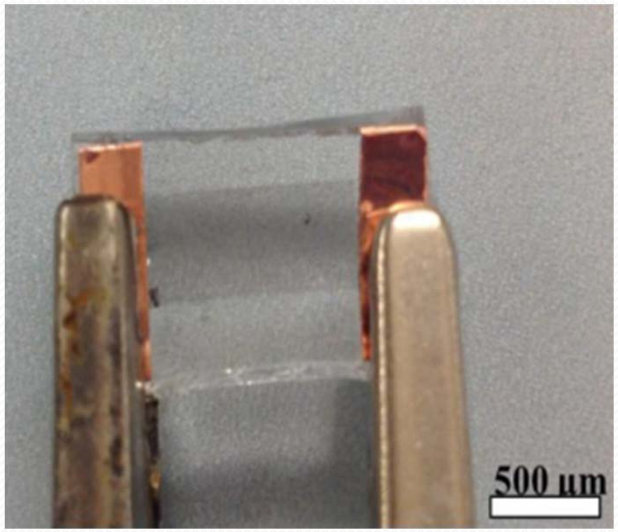
- Individual CNTs



- CNT Fibers

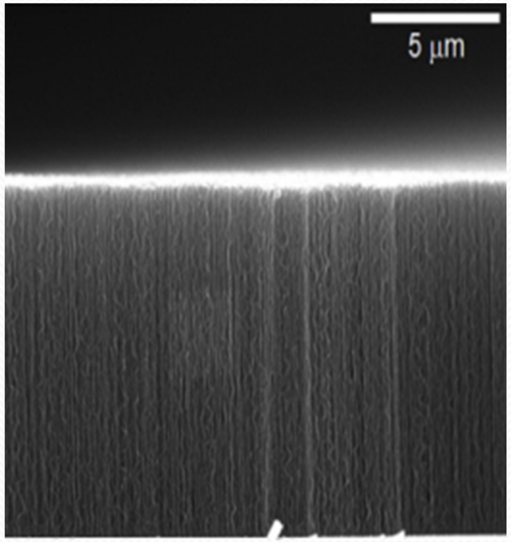


- CNT Film/Paper



Lee, et al. J Kor Phys Soc, 2012

- CNT Array



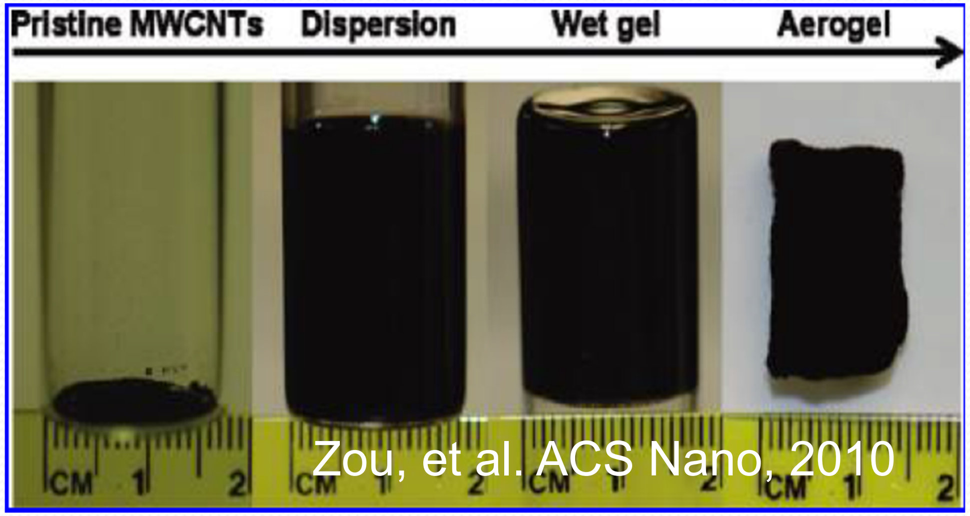
Eom, et al. Carbon, 2013

- CNT Foam

Li, et al. Nano Res, 2014

CNT Foams– Preparation & Bottlenecks

➢ Sol-gel Method



Zou, et al. ACS Nano, 2010

❖ ***Multi-steps*** using CNTs or functionalized CNTs

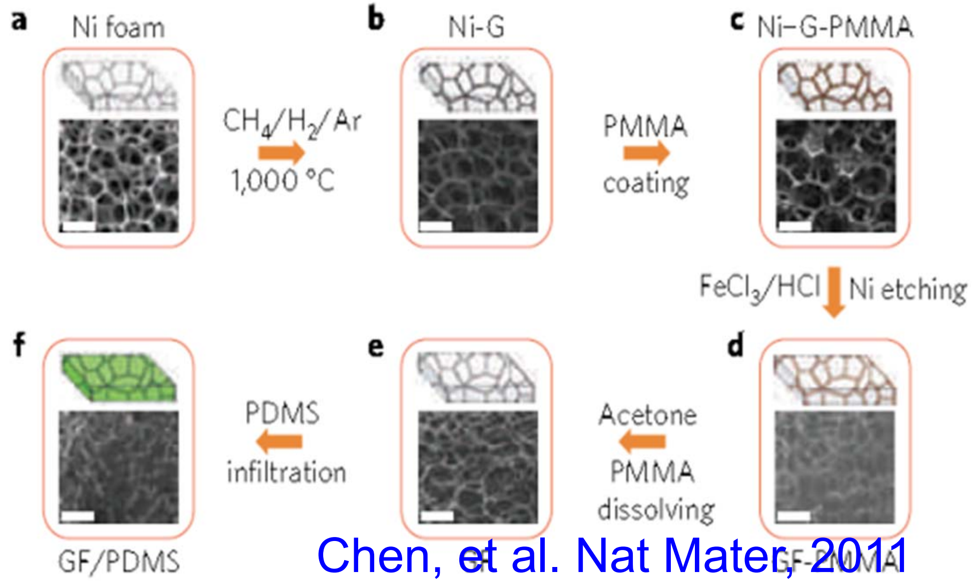
❖ Structural ***instability***

❖ ***Scalable*** production: ??

❖ Material and processing **cost**: ??

❖ ***Frozen-drying*** process

➢ CVD Method



Chen, et al. Nat Mater, 2011

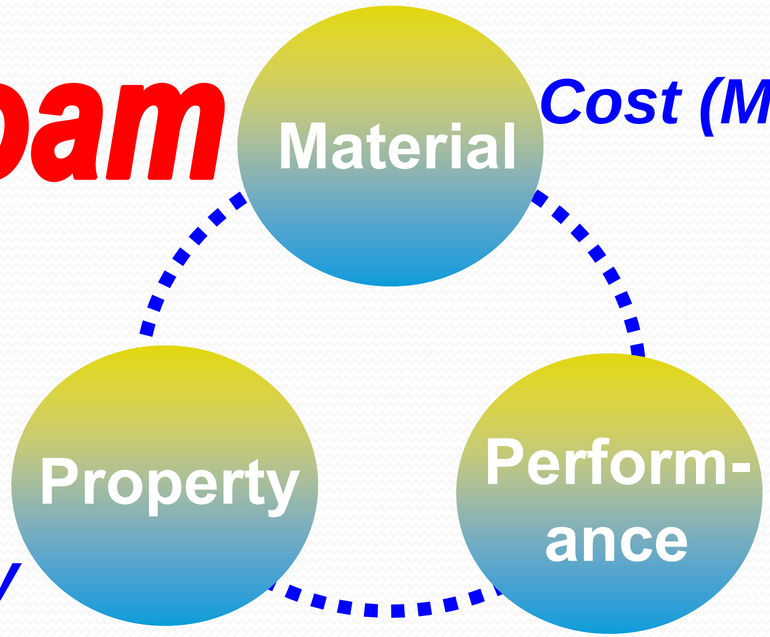
❖ ***Metal foam*** (Cu, Ni, etc) as template

❖ ***High Temp***: 1000 ^{o}C

❖ ***Removal*** of template using acids: ***Negative effects*** on the properties of CNTs

Research Objectives

CNT Foam



Cost (Materials, preparation) & Scalability

Adsorption capacity & Applicability

Structural stability

- **How to realize?**

  -- Polymer as template for CNT growth

  -- Controlled parameters on CVD process

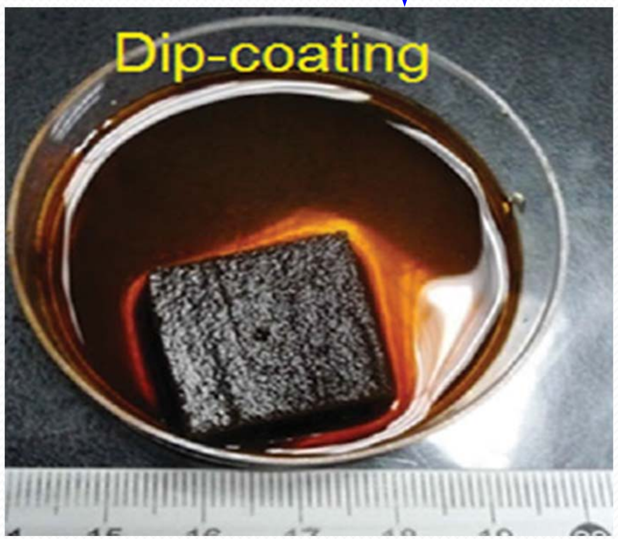
  -- Preparation of CNT/polymer nanocomposites using monomer infusion

Experimental Setups (I)

Immersion in Fe^{3+}/H_2O solution

CVD using C_2H_2, 800 °C

PDMS infusion and curing @ 80 °C

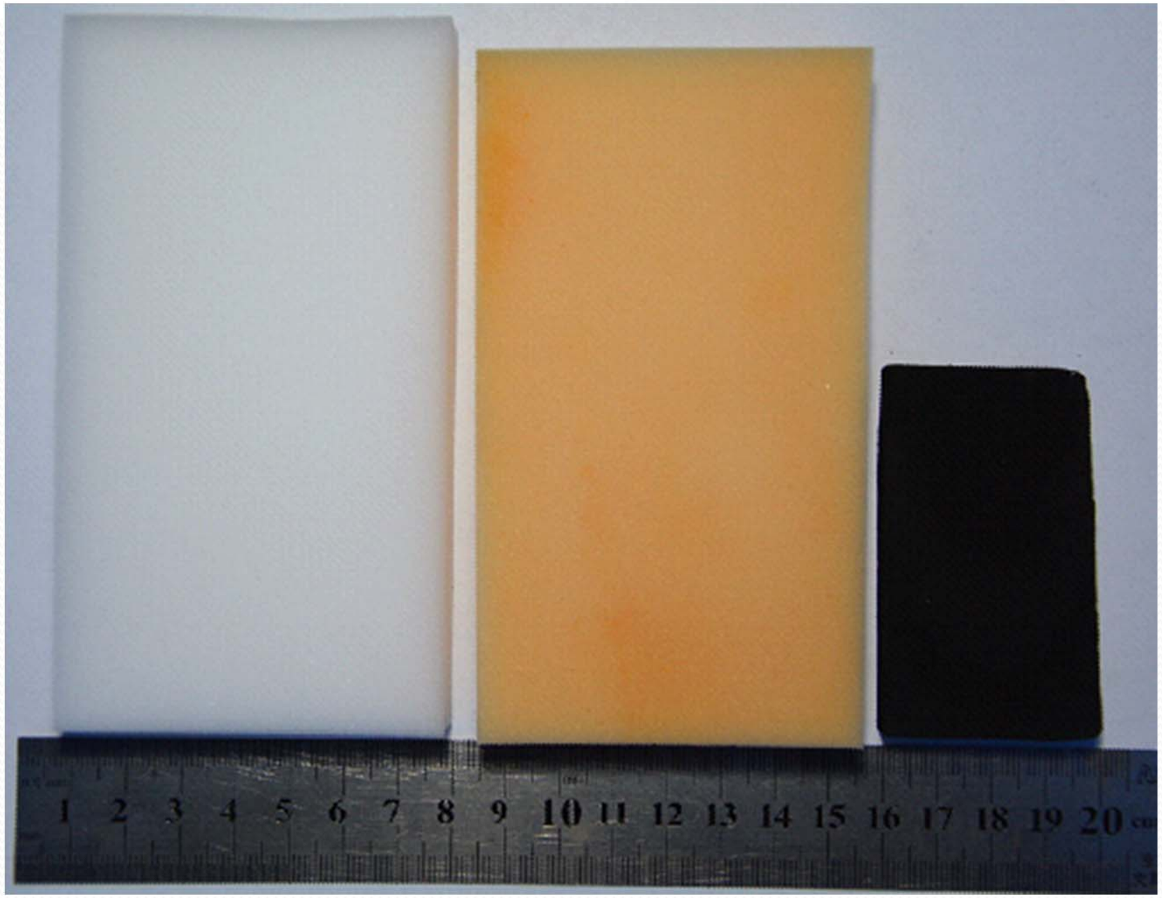


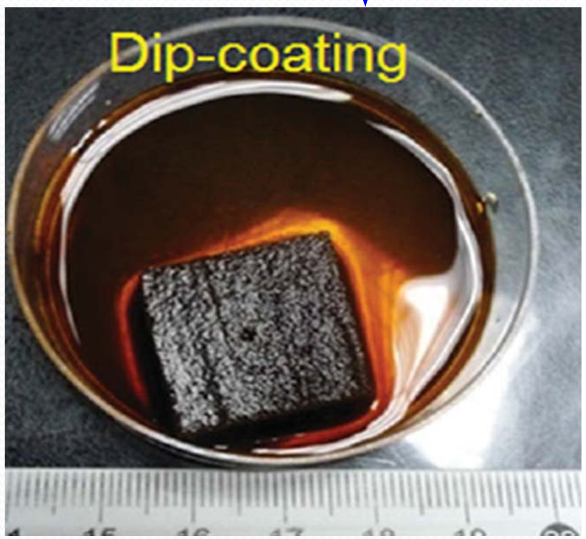
Experimental Setups (II)

Immersion in Fe^{3+}/H_2O solution

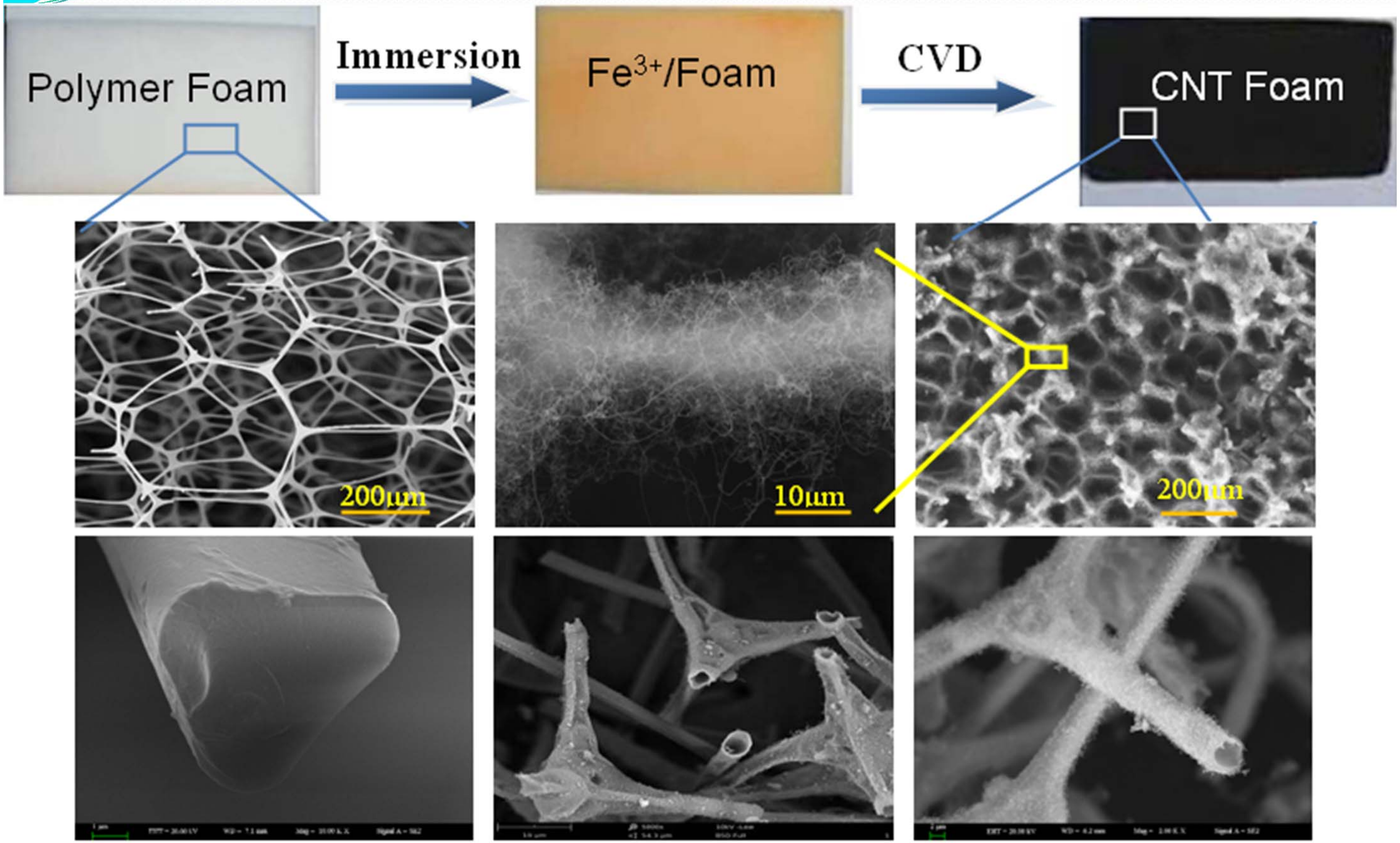
CVD with C_2H_2, 800 ^oC

PDMS infusion and curing @ 80 ^oC



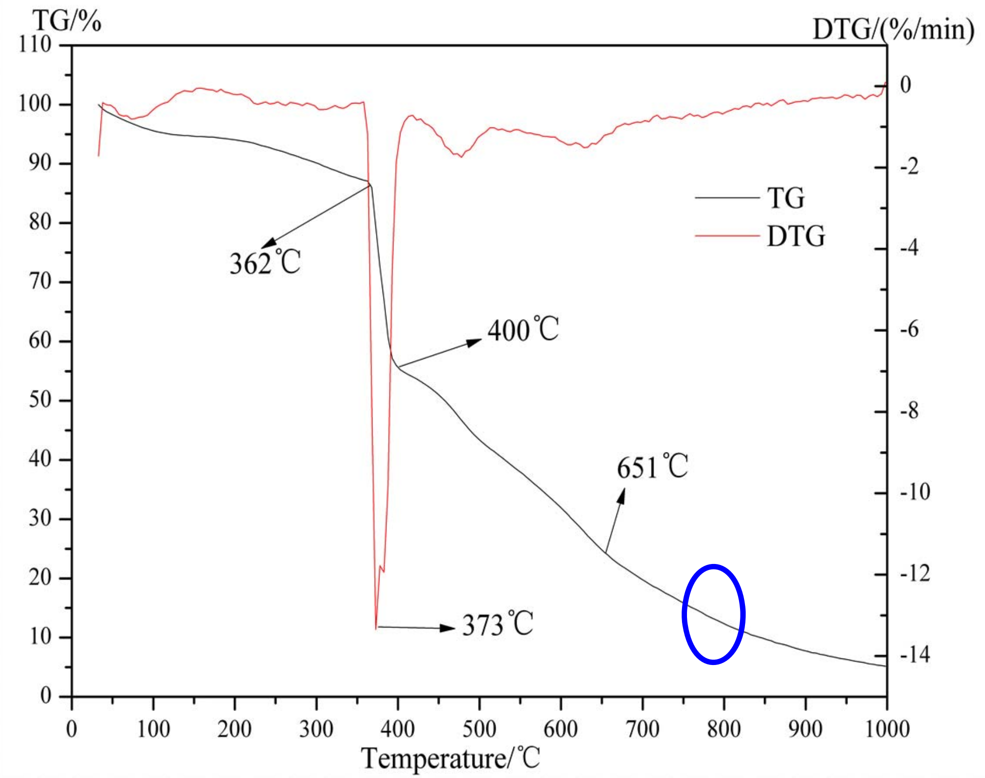


Morphologies of CNT Foam

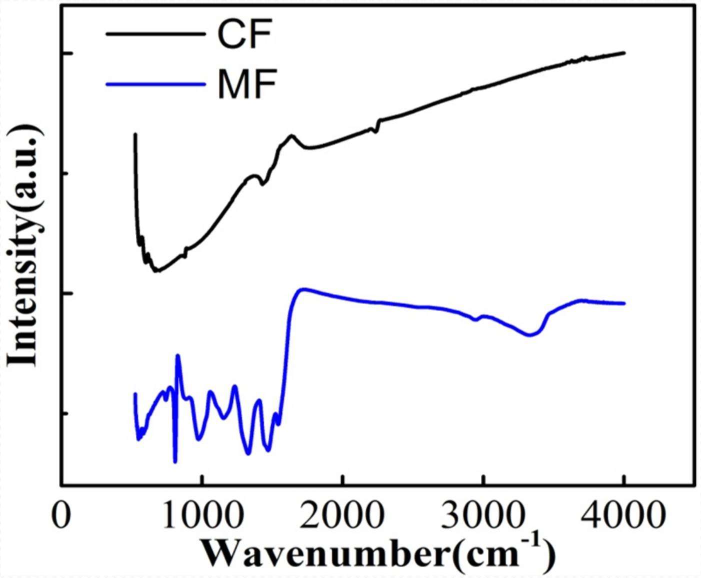


What Happens & Mechanism?

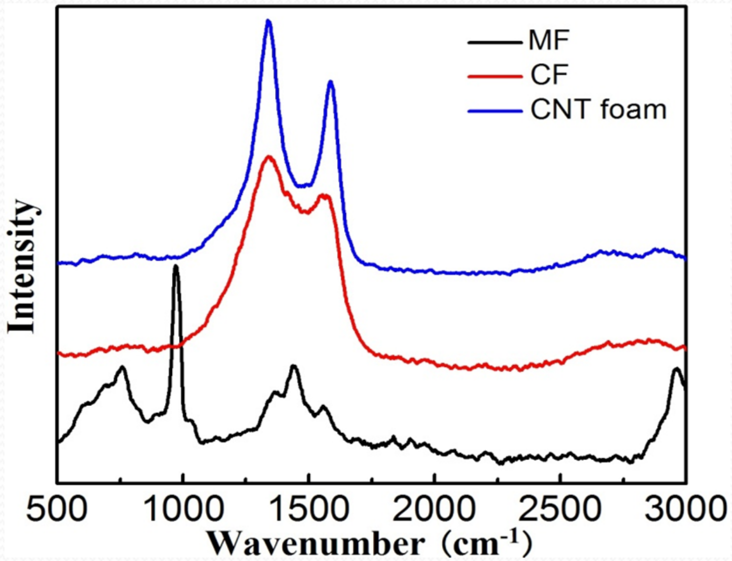
➢ TGA



➢ FT-IR



➢ Raman

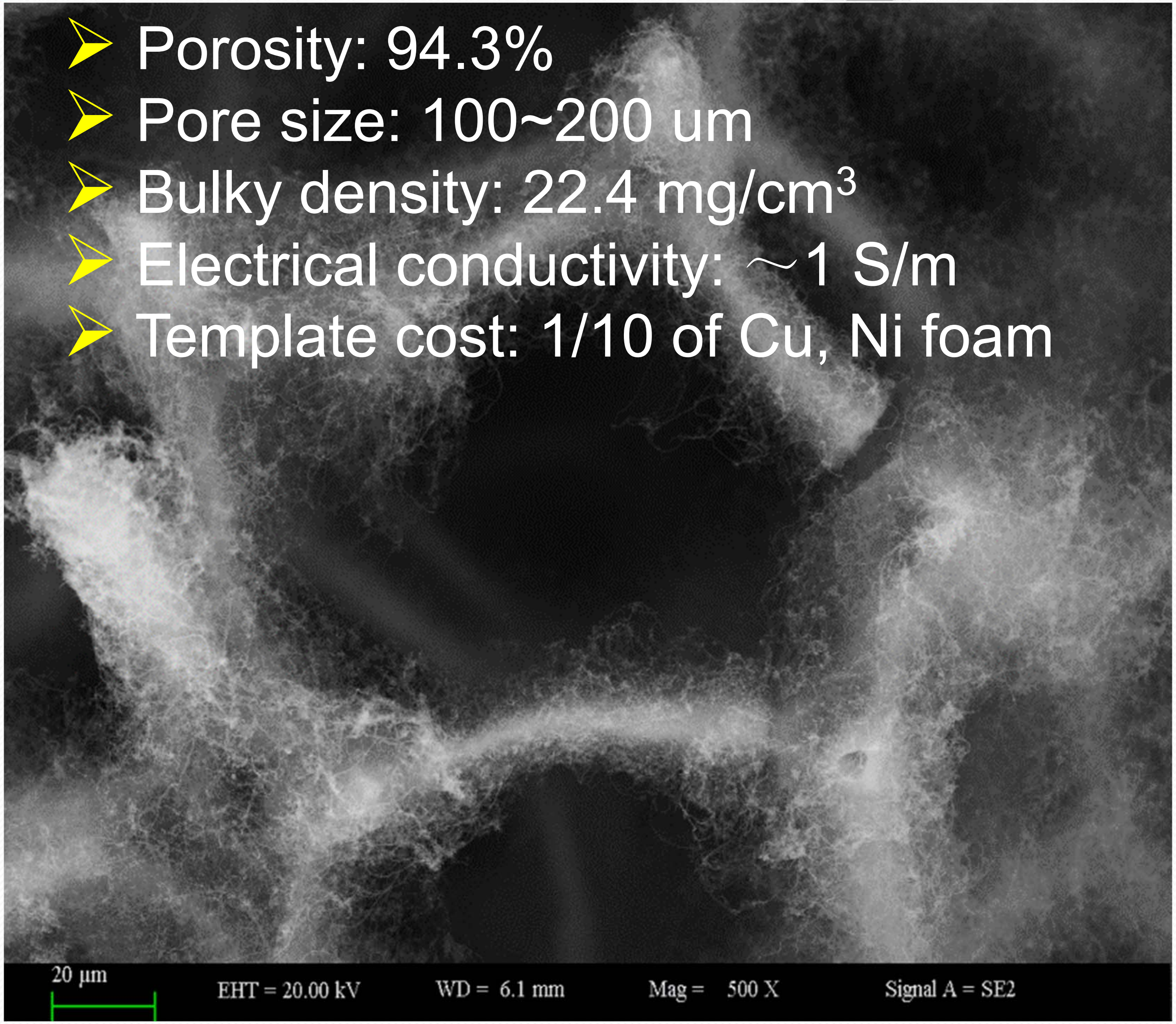


- Decomposition of polymer foam
- Generation of Fe catalyst
- Growth of CNTs

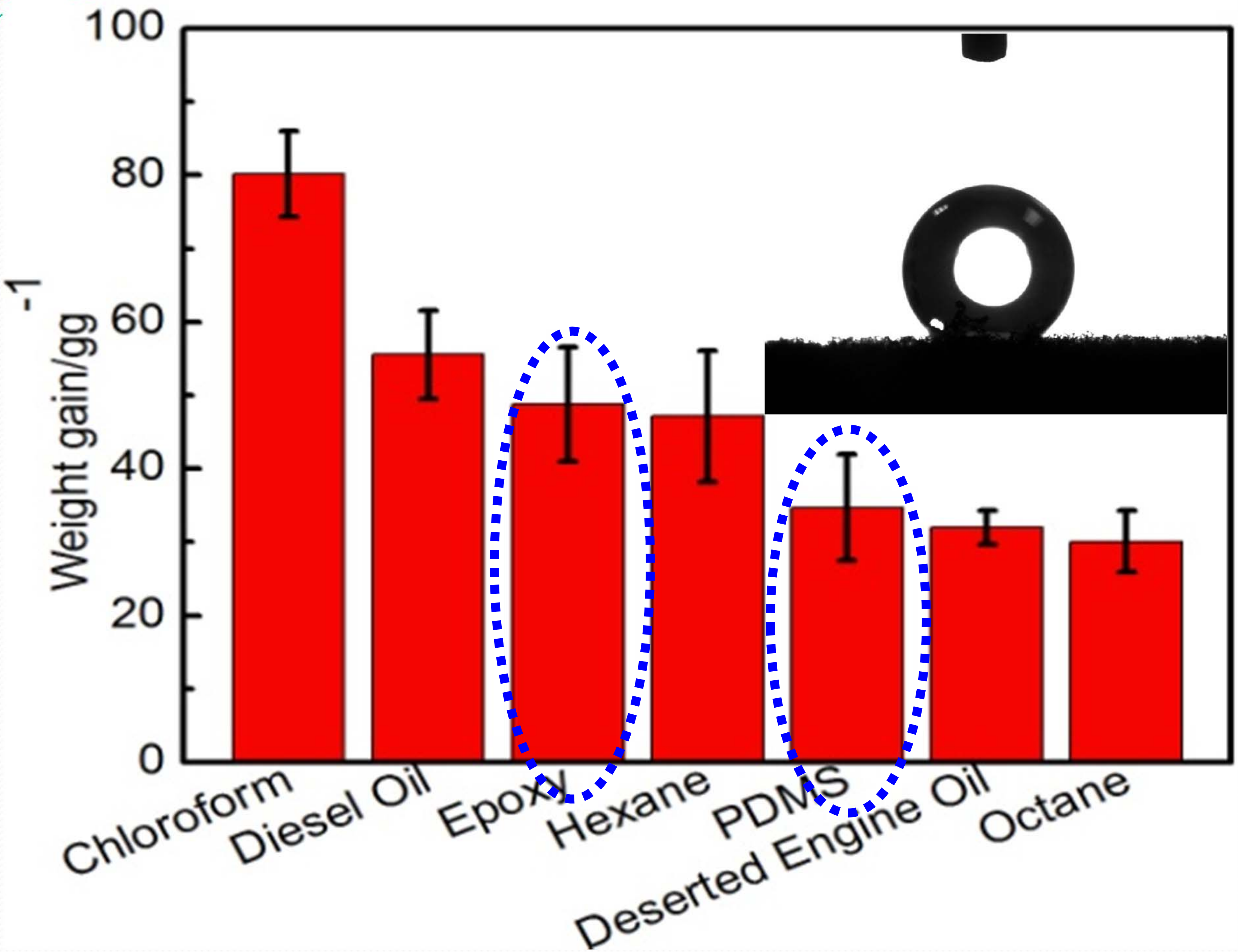
3-in-1 Step

Properties of CNT Foam (I)

- Porosity: 94.3%
- Pore size: 100~200 um
- Bulky density: 22.4 mg/cm^3
- Electrical conductivity: ~1 S/m
- Template cost: 1/10 of Cu, Ni foam

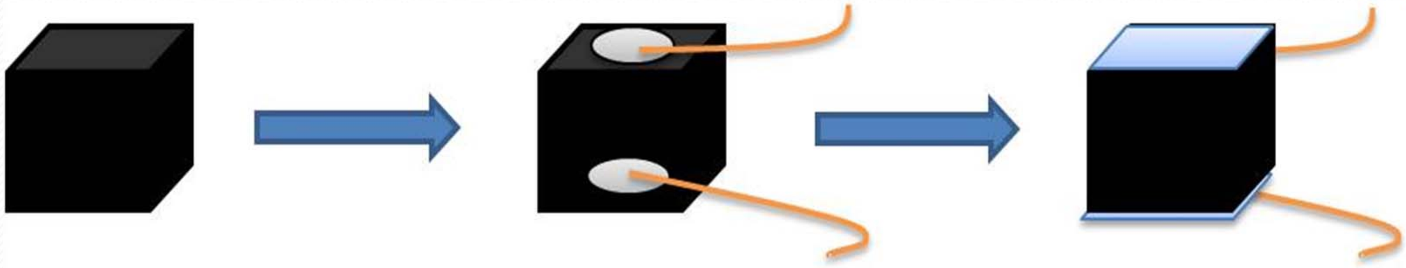


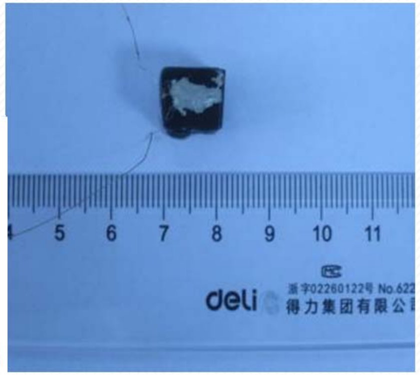
Properties of CNT Foam (II)



CNT Foam (CNT-F)/Polydimethylsiloxane (PDMS) Nanocomposites

➢ Electrical properties

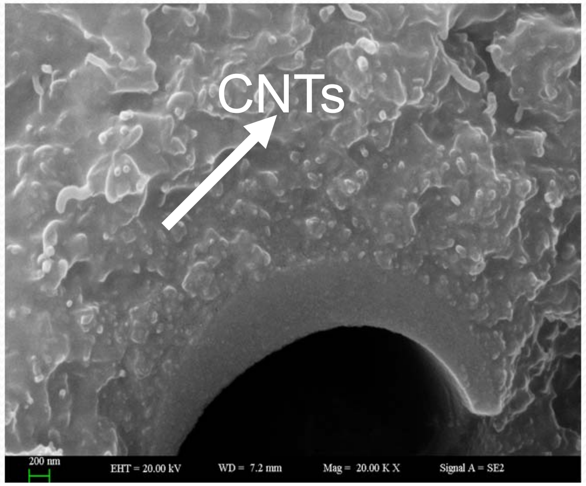


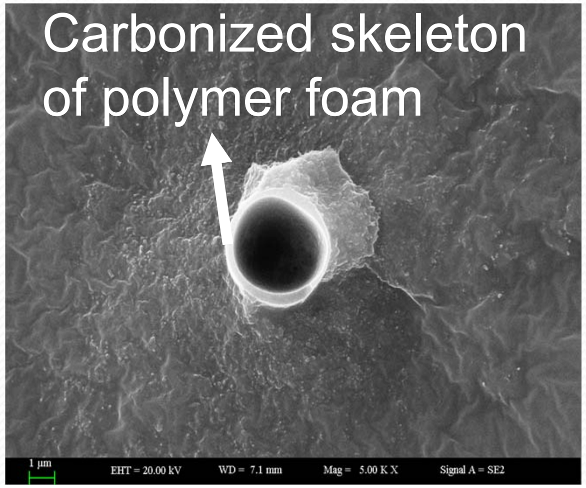


Sample	Electrical conductivity (S/m)
PDMS	$<10^{-10}$
CNT-F/PDMS	~ 1

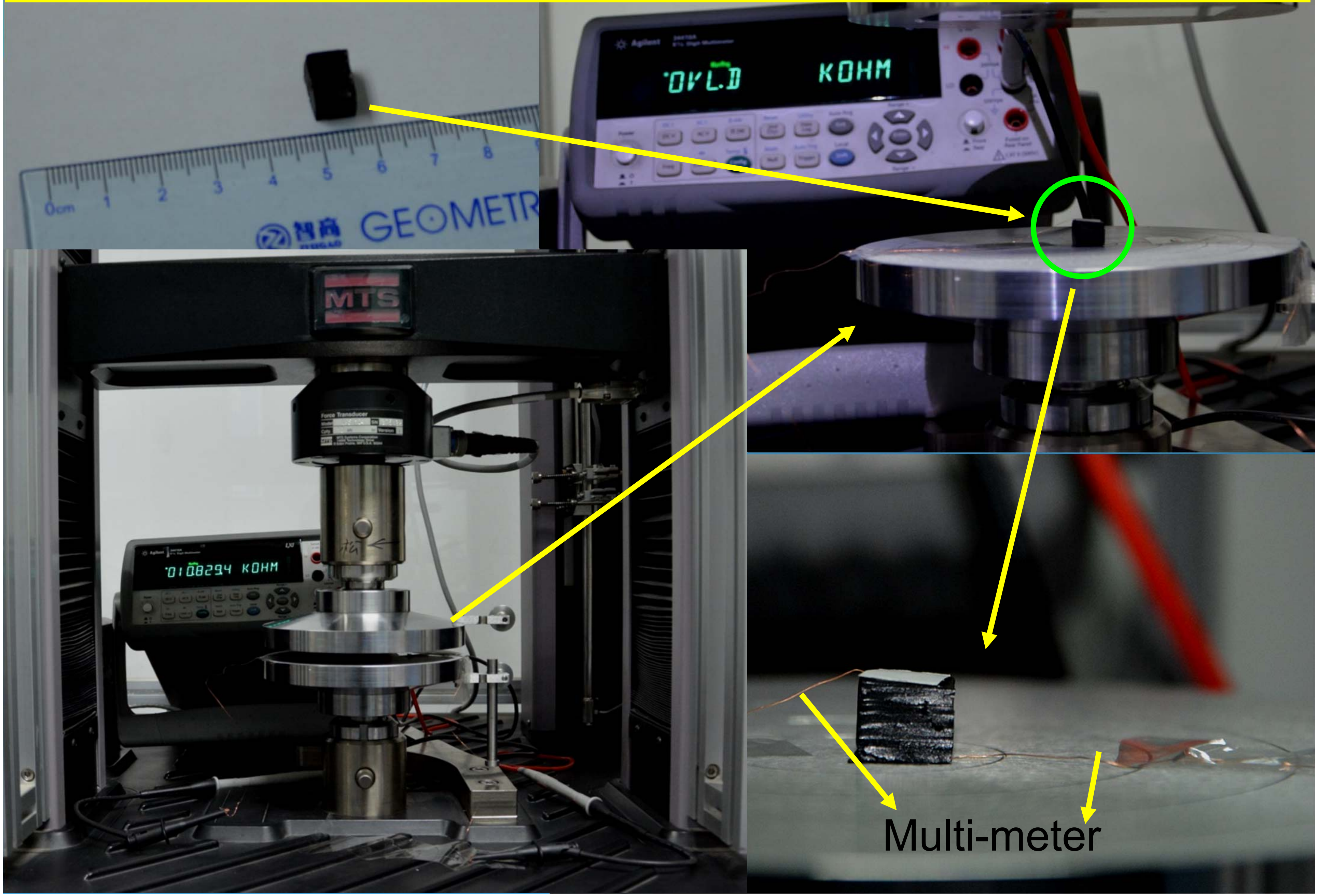
➢ Morphology

Excellent polymer infusion into CNT foam



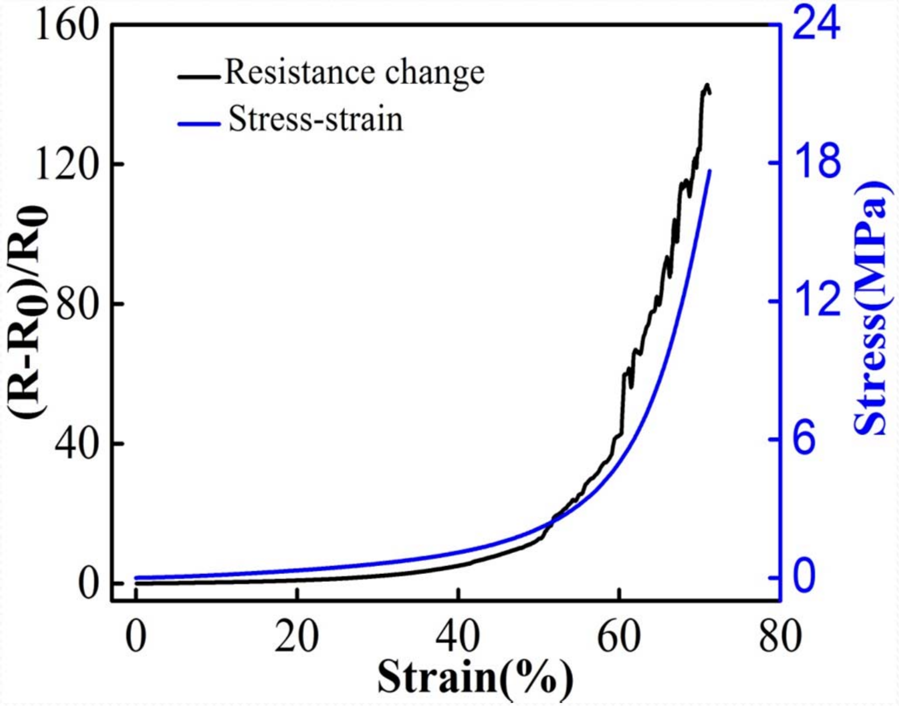


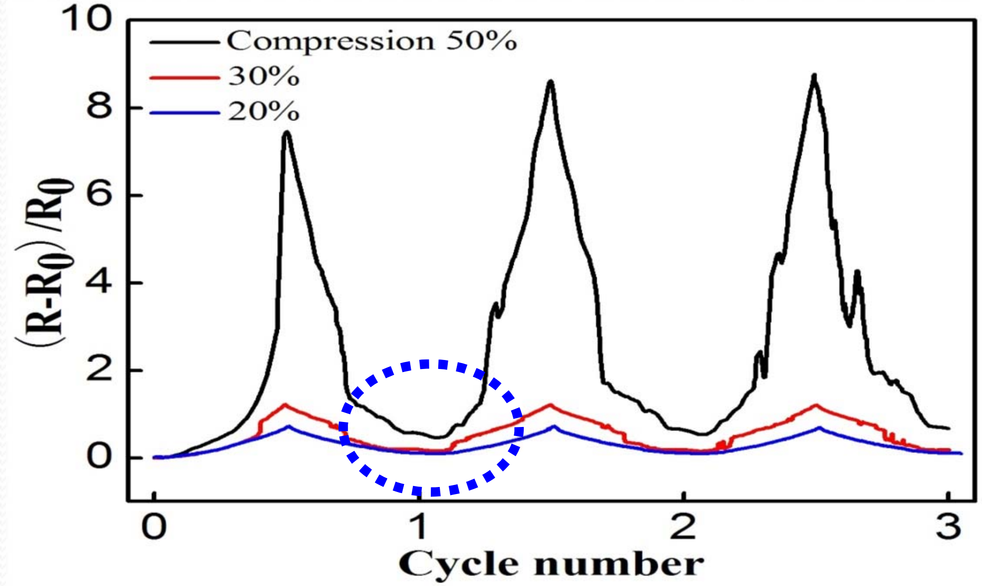
Piezoresistive Effect in CNT-F/PDMS



Piezoresistive Effect in CNT-F/PDMS

➢ R Change Vs. Strain





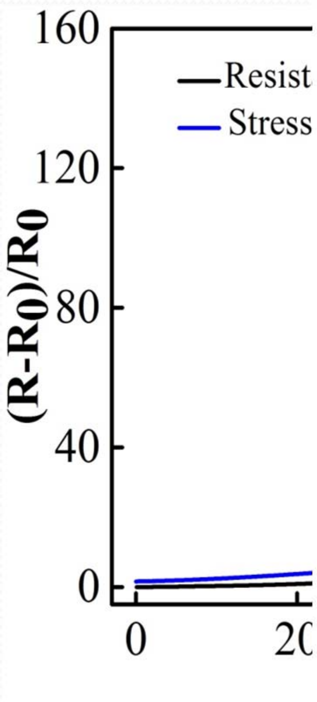
Compression	20%	30%	50%
$R_{residual}$ /R_0	9%	18%	45%

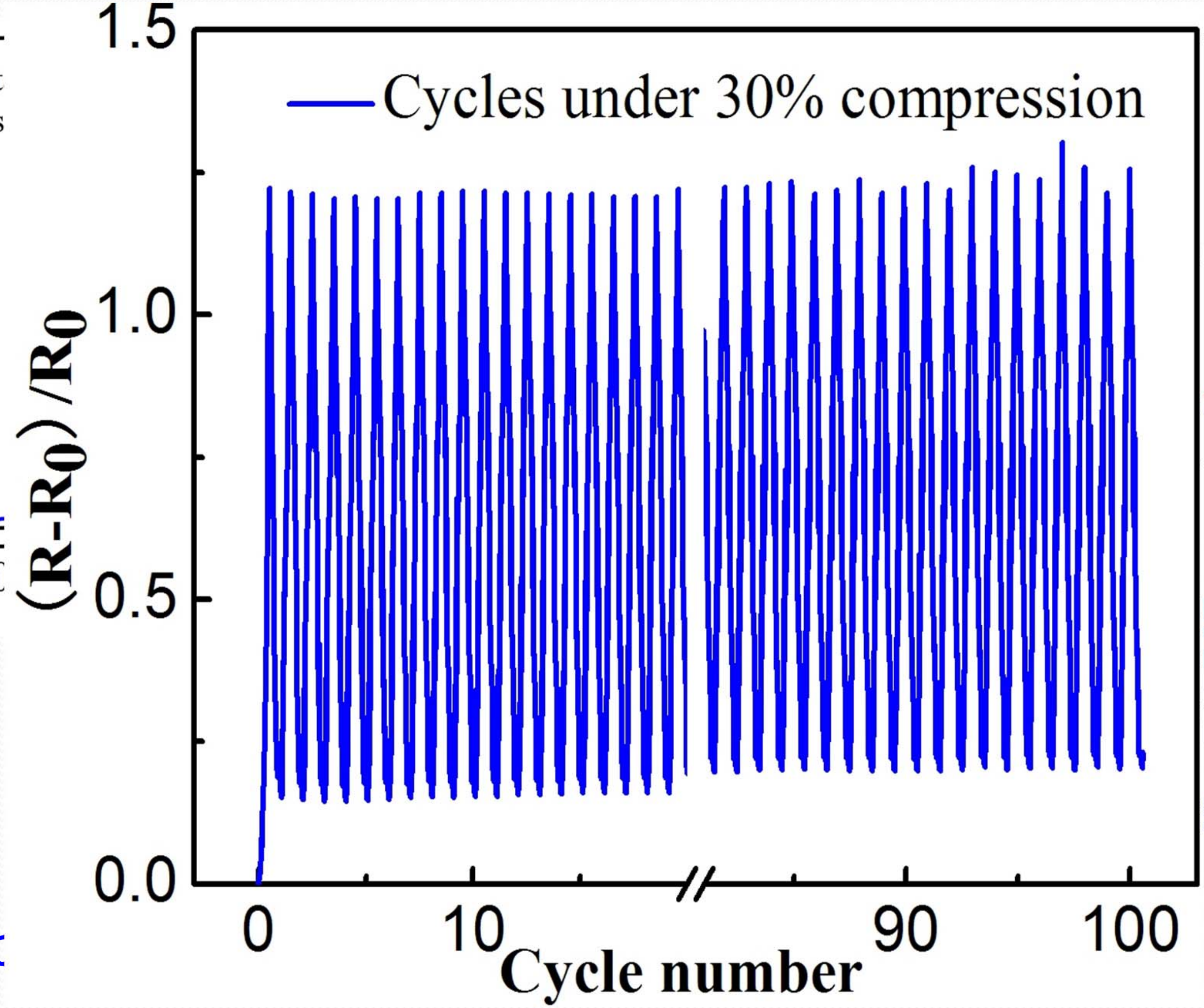
-- Linear Resistance change under low (<30%) and high strain (50%)

-- Significant R change under high strain (50%)

Piezoresistive Effect in CNT-F/PDMS

- R Change Vs. Strain



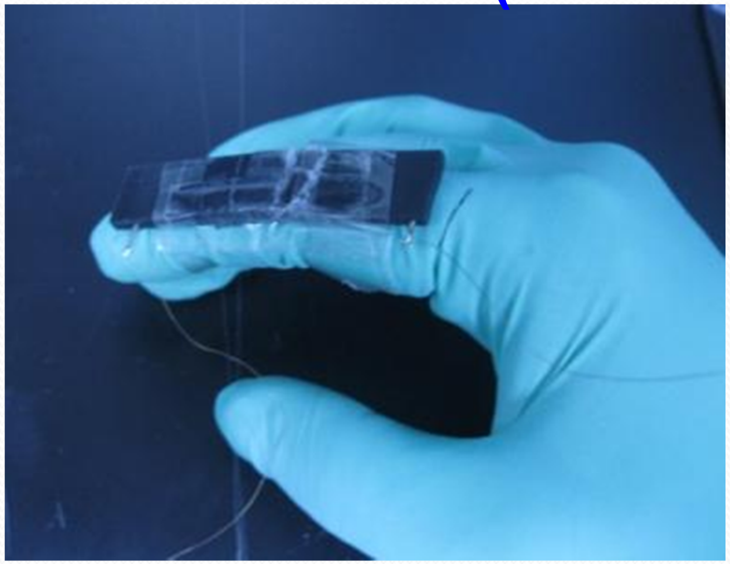


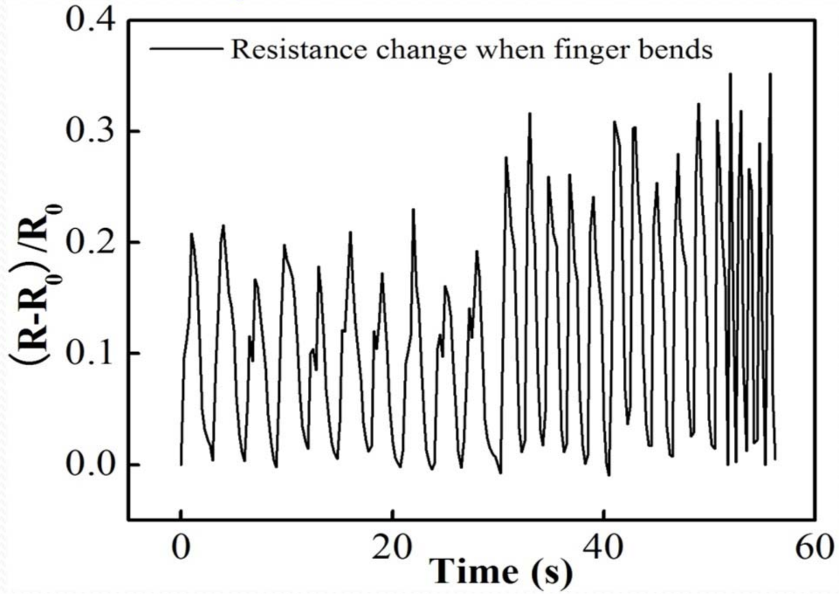
%	50%
%	45%

-- Linear strain
(50%)
-- Signific

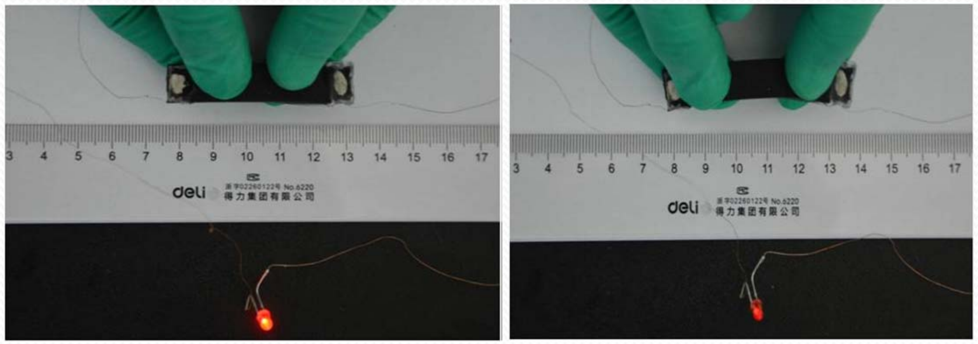
Prototype Sensor based on CNT-F/PDMS

➢ **Motion Sensor (Electronic skin)**





➢ **Motion Sensor (In a Circuit)**



Perspectives

- Mechanical Reinforcement to the Polymers

Sample	Strength (MPa)
PDMS	2.25
CNT-F/PDMS	2.07

- What happens and Mechanism?
- Fatigue properties?
- Optimization on the structure and properties of CNT foam and corresponding
- Fracture behavior under the mechanical loading studied using SEM

Summary

- **3-in-1 step for the preparation of CNT foam**
  -- Polymer as template: Low cost and high scalability
  -- Polymer decomposition; Formation of Fe catalyst and CNT growth

- **CNT/PDMS nanocomposites**
  -- Preparation: Polymer infusion process
  -- CNT dispersion: Excellent thermal stability
  -- Excellent electrical conductivity: Marginal effect from polymer infusion

- **Application of CNT/PDMS nanocomposites:**
  -- Piezoresistive effect under mechanical strain
  -- Prototype sensor by utilizing CNT-F/PDMS

Fundamental issues of CNT/polymer nanocomposites

Ag@CNT/Polymer Nanocomposites

Metal Nanoparticles/CNT Nanohybrids

- **Why CNTs?**

  -- Structure: Rolled up cylindrically in nm scale

  -- Aspect ratio > 1000 (Length/diameter)

- **Metal Nanoparticles/CNT hybrids**

  -- Pt, Au, Fe, Ni, Pd……

- **Silver decorated CNTs (Ag@CNTs)**

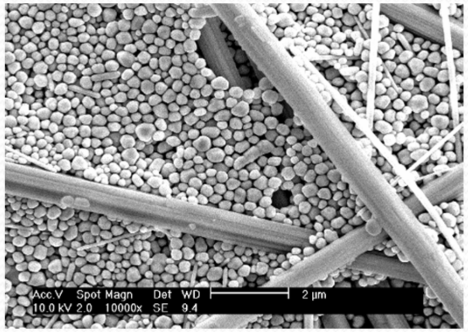
  -- Wide applications: catalyst, optical limiters, advanced materials…..

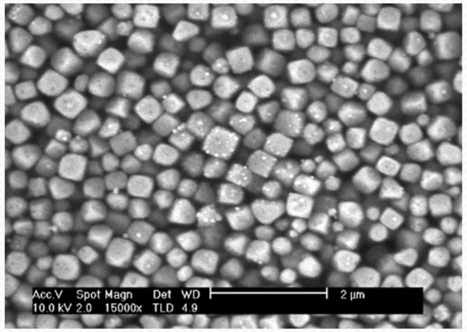
- **Challenges**

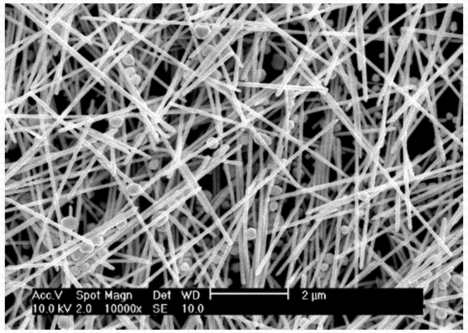
  -- Weak interactions between Ag nanoparticles (Ag-NPs) and pure CNTs. Ag-NPs insertion into the CNTs due to capillary effect

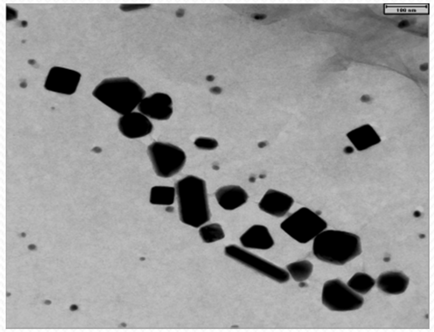
  -- Agglomeration of Ag-NPs

- **To realize effective production of Ag@CNTs, an easy and low-cost route is desired.**





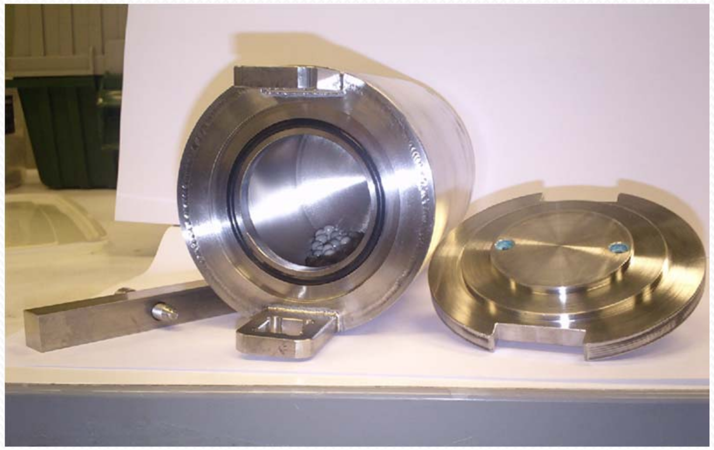




Ag@CNTs Preparation

➢ **Optimized Processing Condition**

CNTs → A → Functionalized CNTs → B → Dispersed CNTs → C → Ag@CNTs

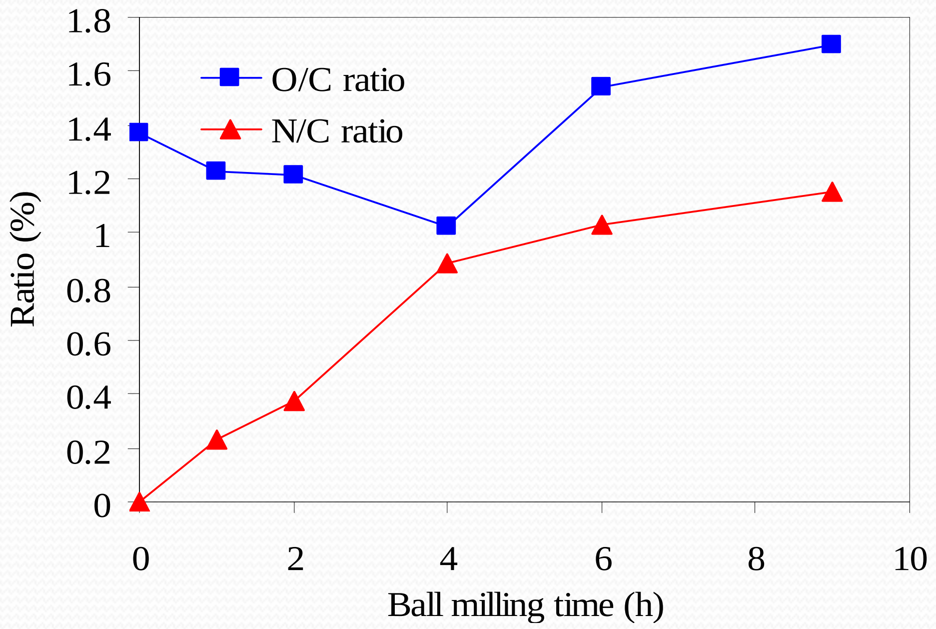


A: Ball milling with NH_4HCO_3 for 4 h (Mechanico-chemical functionalization)

B: Ultrasonication for 1h

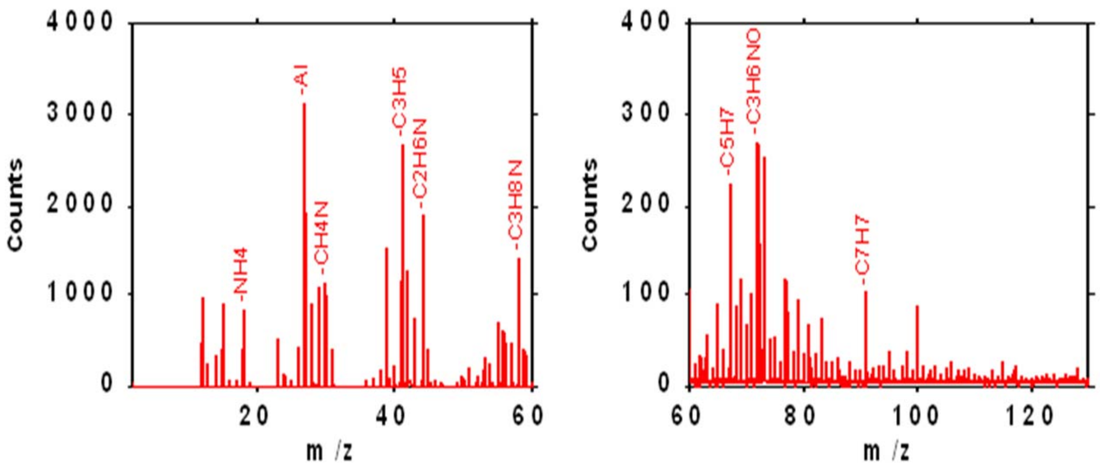
C: Ag^+ reduction by *N*,*N*-dimethylformamide (DMF)

Elemental Compositions and Surface Chemistry of CNTs



- Increase in N/C ratio (by XPS): N attachment on CNT via covalent bonding or physical adsorption.

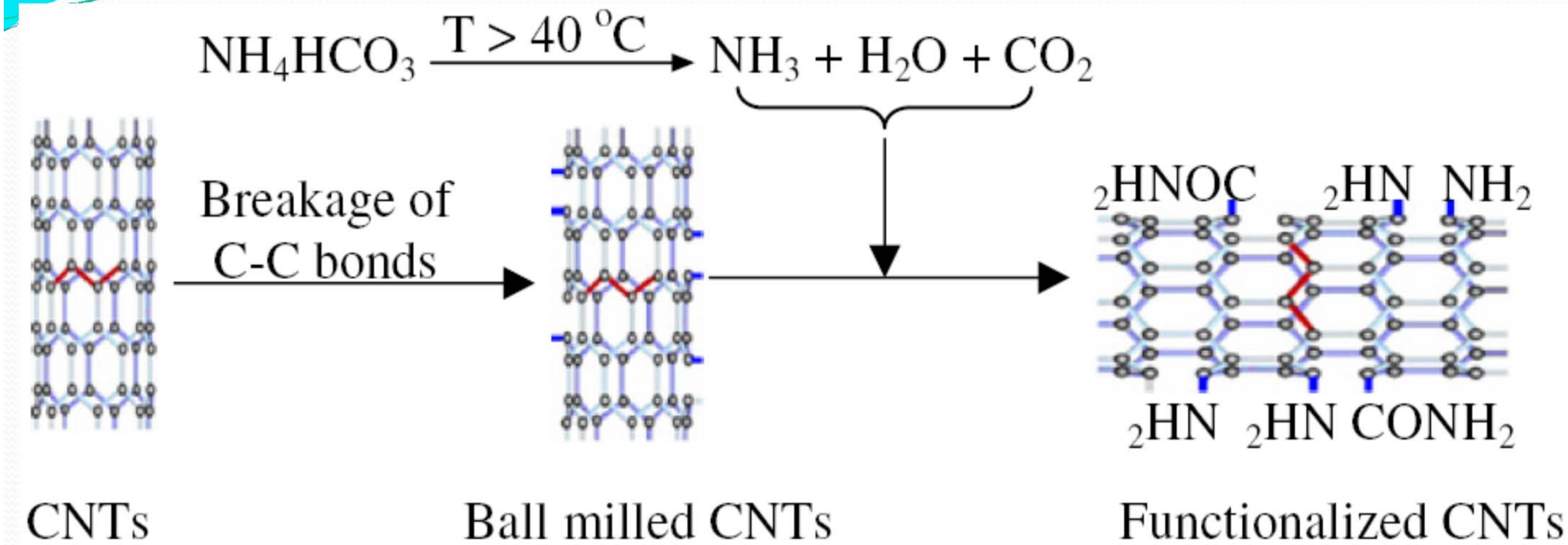
- Pristine CNTs: high O/C ratio of 1.37%, moisture or oxidation during CNTs purification



ToF-SIMS results of CNTs after 2 h of milling

- **Three N compounds**:
m/z=18: NH_3 gas absorbed on CNT;
Amine: $–CH_4N$, $-C_2H_6N$ and $-C_3H_8N$;
Amide: $-C_3H_6NO$ ($-CH_2CH_2-CO-NH_2$).

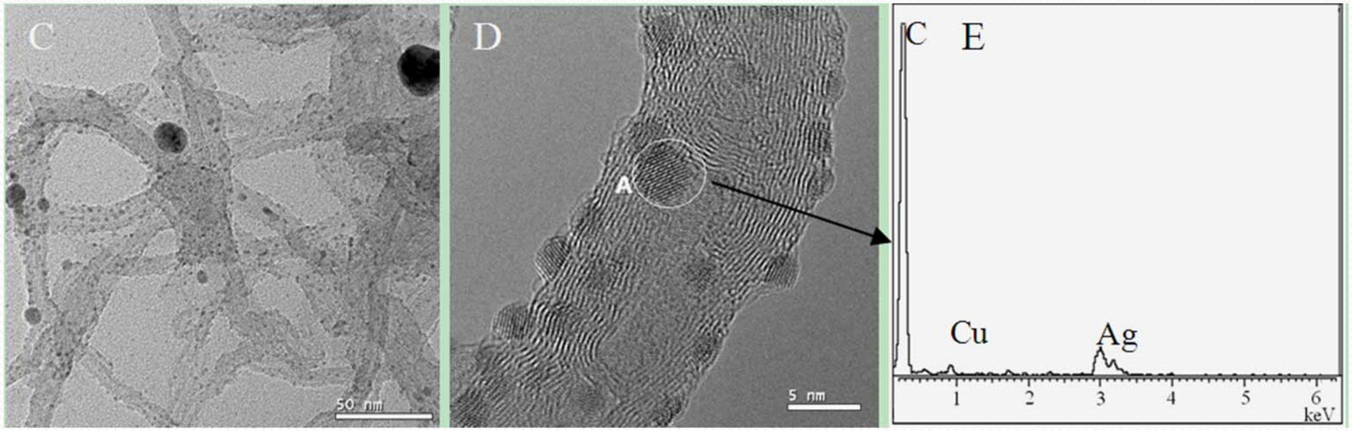
Mechanism



- During milling, NH_4HCO_3 is decomposed into NH_3 gas, H_2O and CO_2.
- The ball milling process breaks the –C–C– bonds on CNT surface.
- Amine and amide groups to form covalent bonds with the broken –C–C– bonds of the CNT surface.

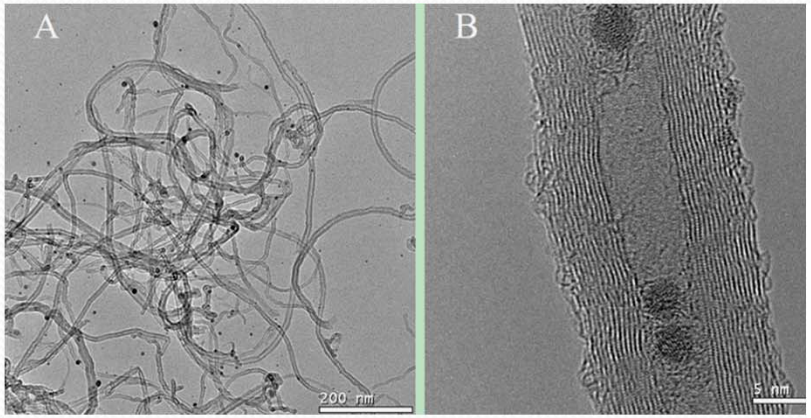
Interactions between Ag and CNTs

- **CNTs with ball milling**



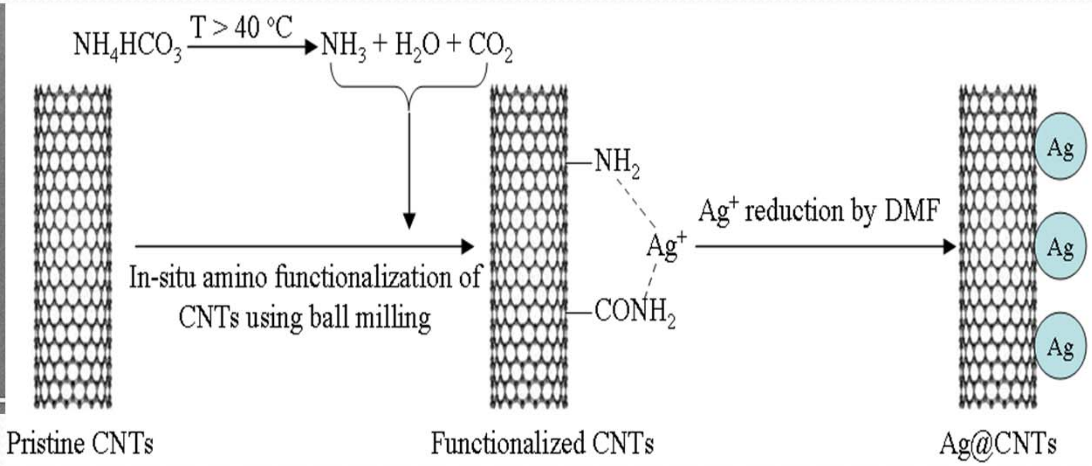
Uniform distribution of Ag-NPs onto CNTs without agglomeration; Ag-NPs: 2-4 nm.

- **CNTs without ball milling**

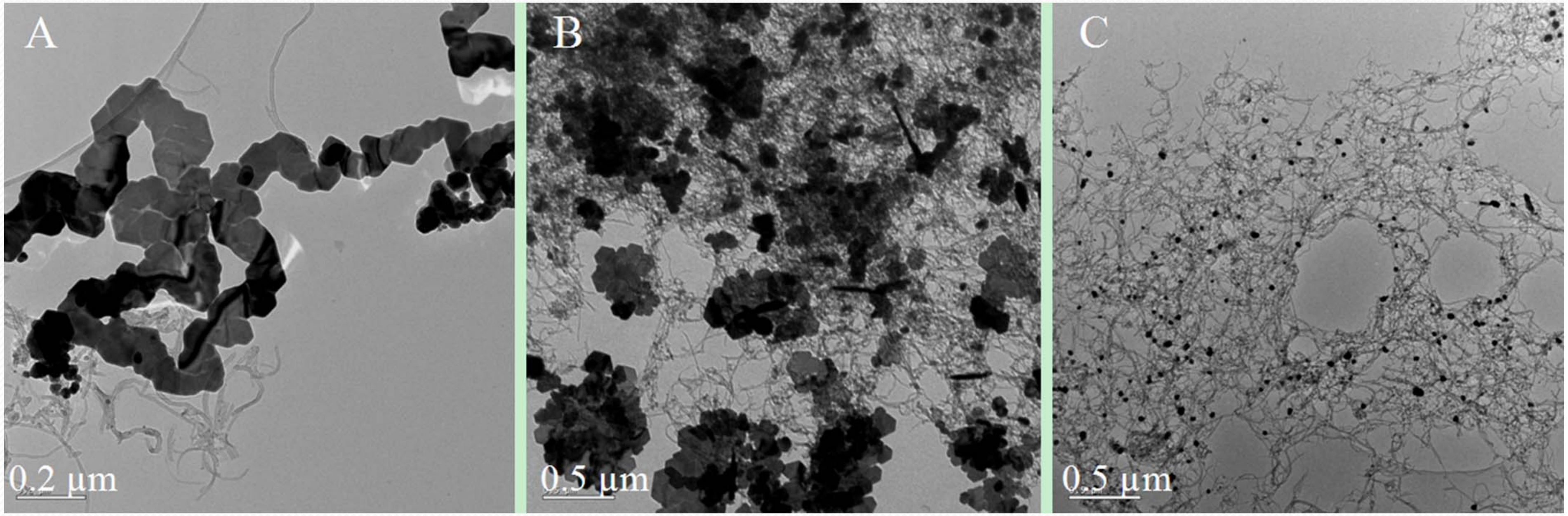


Ag-NPs inside the tubes

- **Mechanism**



Influence of pH Value on Ag Decoration

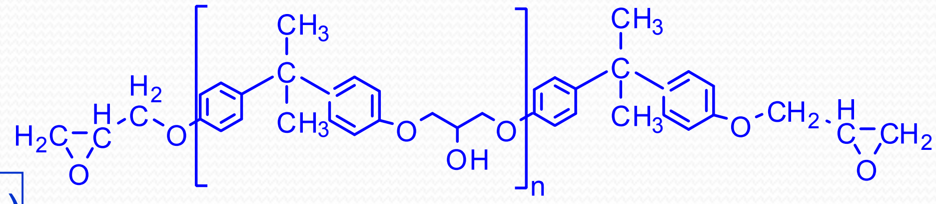


pH=2 **pH=4** **pH=6**

- pH=2, individual Ag nanowire
- pH=4, hexagon Ag-NPs and particles agglomerattion
- pH=6, spherical Ag-NPs attached tightly onto CNTs

Ag@CNT/Epoxy Nanocomposite

➢ Nanocomposite Fabrication



Epoxy (DGEBA)

Degassing at 80 ℃ for 2h

CNT

Disperse in ethanol

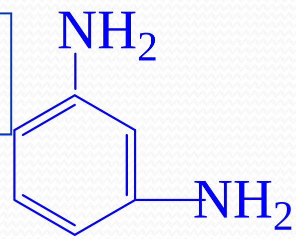
Sonicated mixture

1. Ultrasonic at 60℃ for 1h
2. Ultrasonic at 80 ℃ for 1h

Vacuum oven at 80℃ for 5h

1. Curing at 80℃ for 2h
2. Curing at 150 ℃ for 2h

Curing agent (m-PDA)
(14.5 wt% of epoxy)



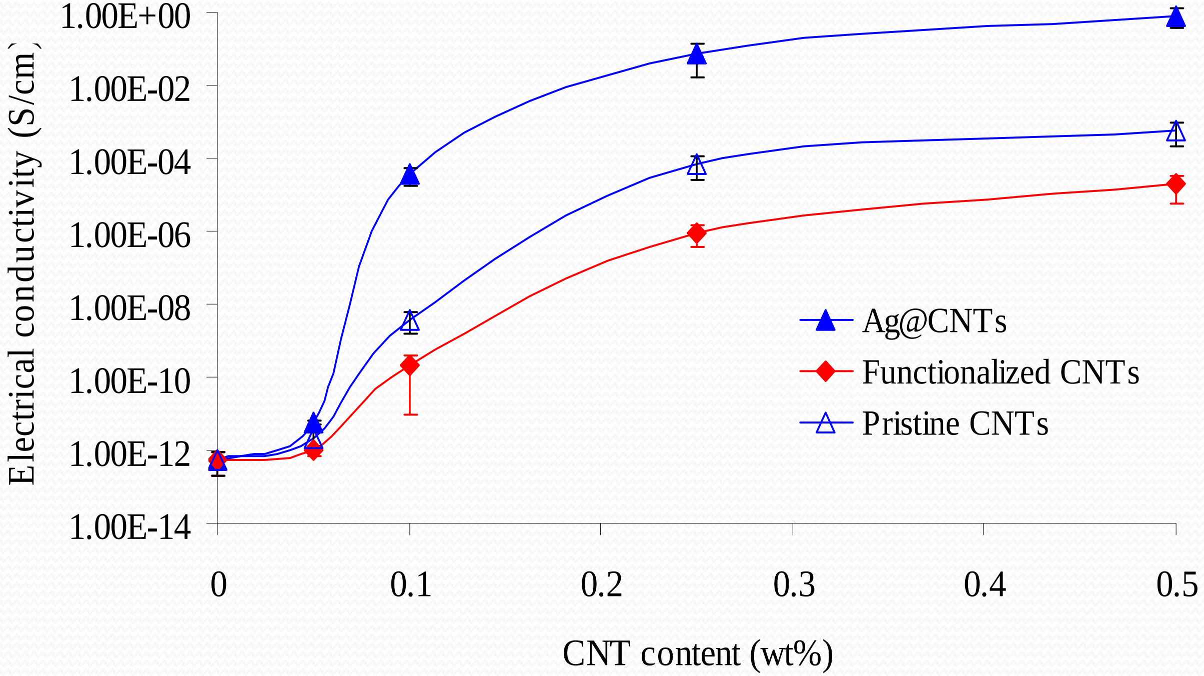
Nanocomposites

Electrical Conductivity of CNTs and Corresponding Nanocomposites

➢ Electrical Conductivities of Different CNTs

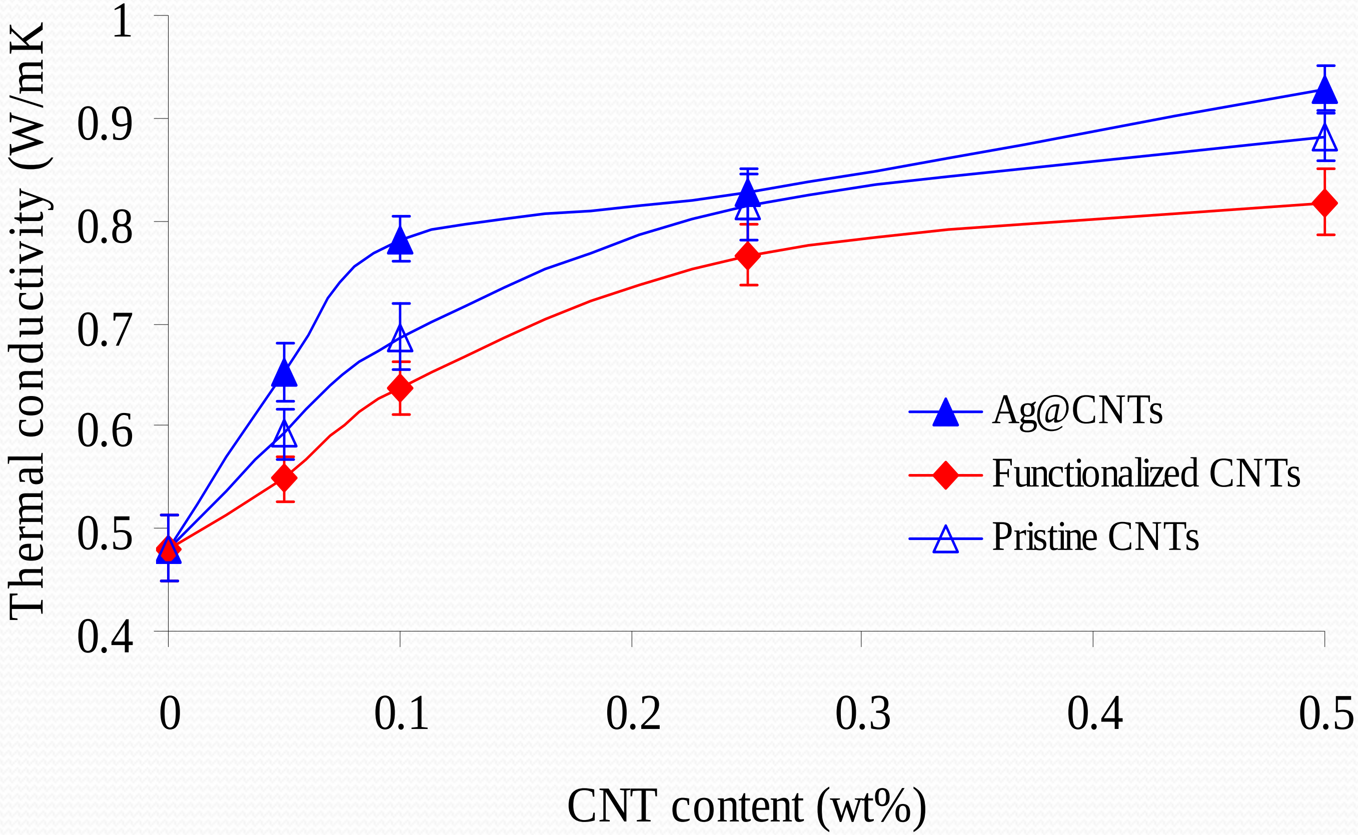
Sample	Pristine CNTs	Functionalized CNTs	Ag@CNTs
Electrical conductivity (S/cm)	5.15±0.57	9.33±0.56	30.53±1.28

➢ Electrical Conductivities of Nanocomposites



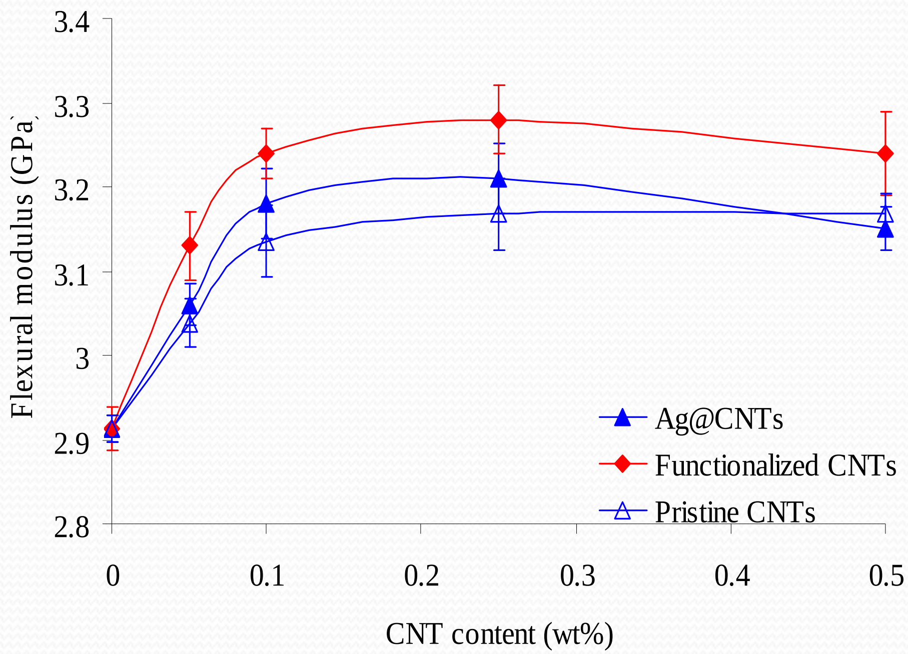
- ➢ All nanocomposites presented the transition from the insulator to conductor;
- ➢ Approximate percolation thresholds: ~ 0.10 wt% CNTs;
- ➢ More pronounced enhancement in EC for Ag@CNT nanocomposites: From 2.2×10^{-13} to 0.81 S/cm when CNT=0.50 wt%.

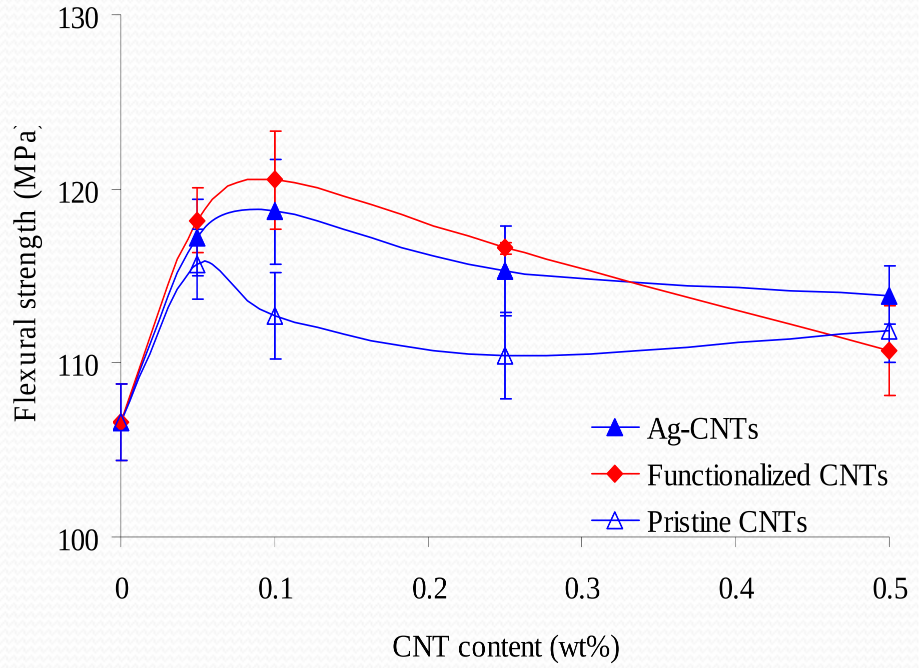
Thermal Conductivity of Nanocomposites



➢ Thermal conductivities: Ascending order of functionalized CNTs, pristine CNTs and Ag@CNTs for a given CNT content. > 30% increase with CNT=0.1 wt%.

Mechanical Properties of Nanocomposites





- Rapid increase in modulus when CNT≤0.10 wt%;
- Peak flexural strength at about 0.05-0.10 wt% CNT, followed by gradual decrease;
- No sacrifice on the reinforcement effect of CNTs after functionalization and Ag decoration.

Summary

- In-situ amino functionalization of CNTs using ball milling
- Nitrogen atoms on CNTs: amine and amide groups, contribution to electrical conductivity

- Amino functionalized CNTs: template to prepare Ag@CNTs;
- pH=6: Well dispersed Ag-NPs on functionalized CNTs
- Significantly higher electrical conductivity for composites containing Ag@CNTs
- Comparable thermal and mechanical properties of the composites with different CNTs

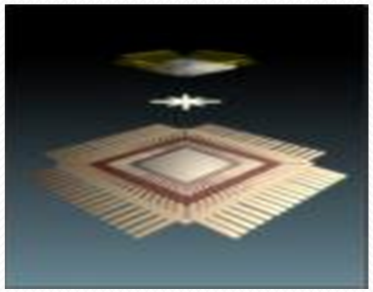
Fundamental issues of CNT/polymer nanocomposites

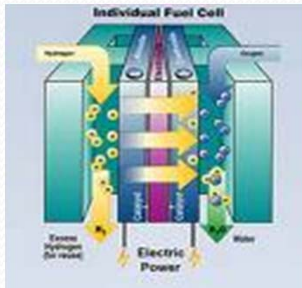
Electrically Conducting Nanocomposites with Hybrid Fillers of CNT and Carbon Black

What is Conducting Polymer Composites?

- **Binary systems, consisting of conducting fillers and polymer matrix**
- **Fillers**
  - -- Metal powder: Cu, Ag, Au, Sn…
  - -- Carbon based materials: carbon black, graphite, carbon fibers ....
- **Features of conducting composites**
  - -- High electrical conductivity (variable depending on filler loading)
  - -- Relatively inexpensive materials
  - -- Improved physical and mechanical properties (light weight, toughness, resiliency, versatility in shaping, corrosion resistance......)
- **Representative applications:**
  - -- Conducting adhesive
  - -- Antistatic layers for electrostatic dissipation
  - -- Electromagnetic and radiofrequency interference shielding
  - -- Aircraft structural materials
  - -- Sensors and actuators
  - -- Photovoltaic coatings, fuel cells and batteries .....

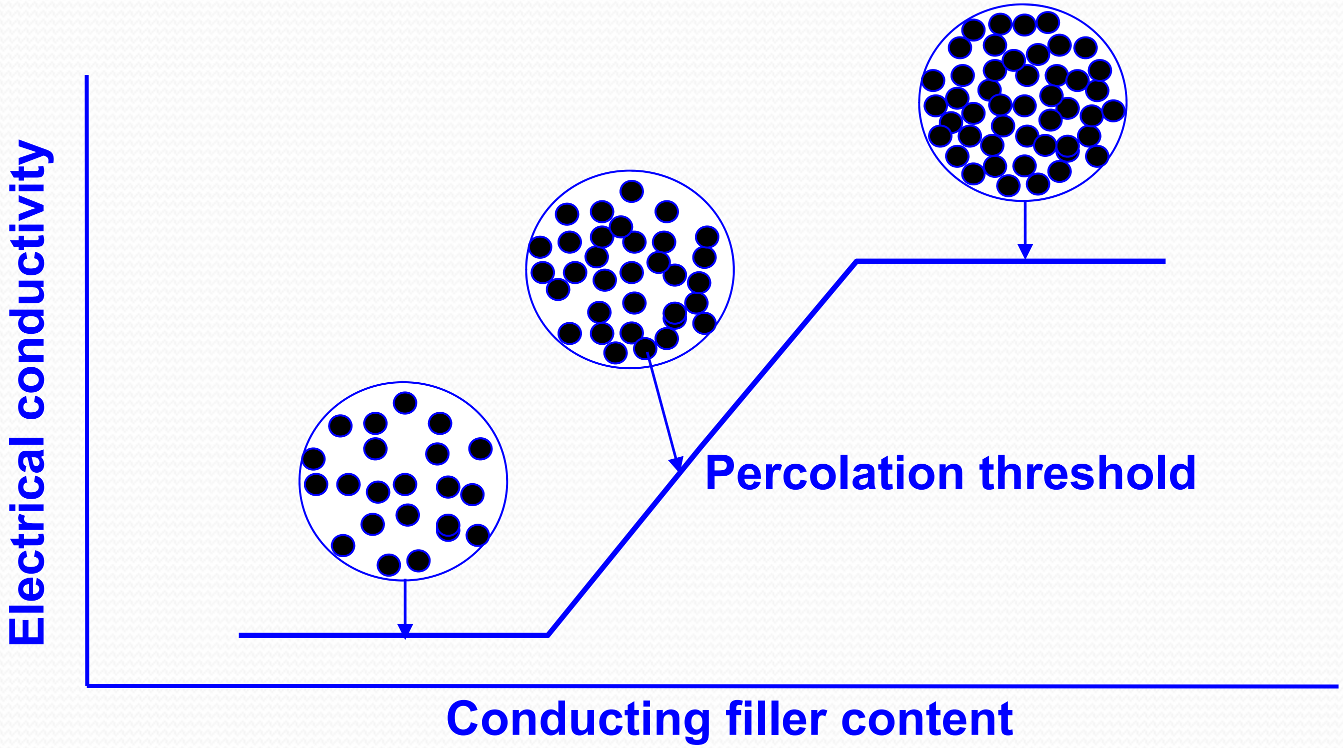






Mechanism for Conducting Composites

➢ **Percolation threshold (Pc)**



➢ With increase in the filler content, the composite undergoes an insulator to conductor transition.

➢ At a critical filler content, the electrical conductivity of composites suddenly jumps up several orders of magnitude

Bottleneck of Conducting Composites

- **Fillers**

  -- Cost, (Ag, Pt…, commercial conducting adhesive: Ag >60%)

  -- Toxicity (Sn, Pb…)

  -- Chemical stability (oxidation, humidity)

  -- Distribution in polymer matrix (Filler diameter, filler/polymer interface)

  -- Amount of conducting filler required to achieve percolation threshold (for the composites with random system > 10 vol%)

- **Polymer matrix**

  -- Processing problems (conducting network formation)

  -- Mechanical properties

- **New fillers to lower the percolation threshold**

  -- To produce adequate conductivity

  -- To minimize problems with mechanical properties

- **Ideal materials for conducting composites**

  -- High aspect ratio and electrical conductivity

  -- Low cost and low loading in composites

Fillers Used in this Study

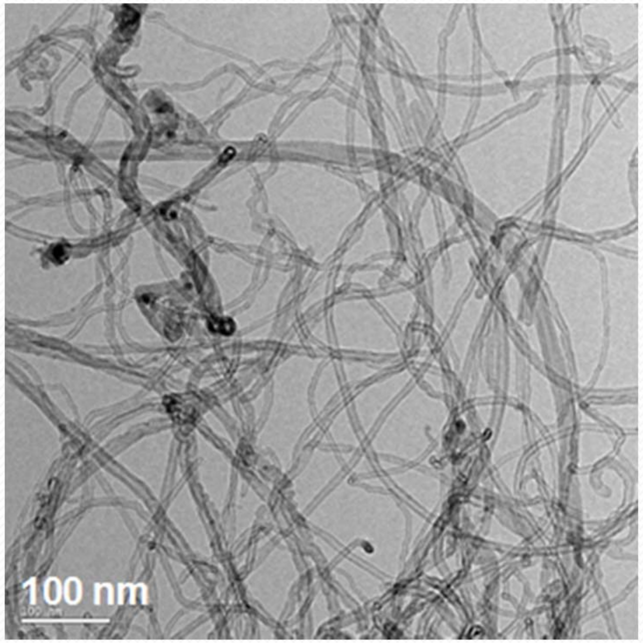
➢ CNTs

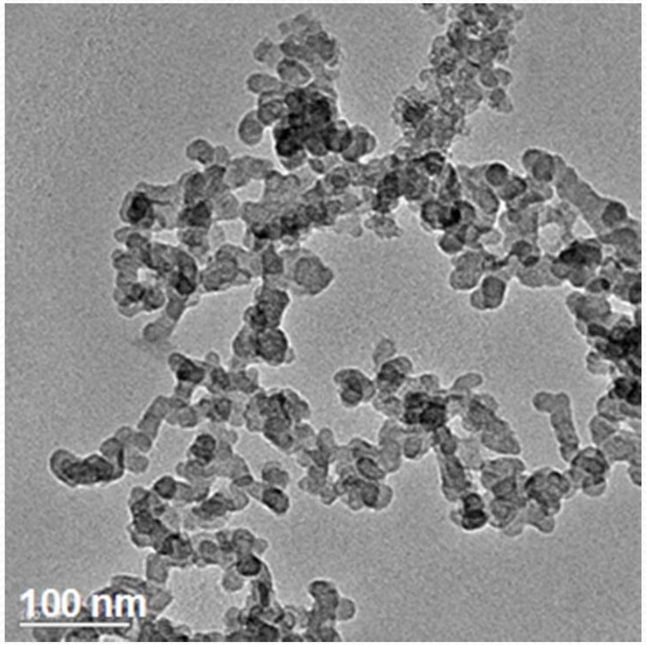
-- Multi-walled CNTs (Iljin Nanotech Ltd., Korea)

-- Produced by CVD (purity over 95%)

-- Diameter: 10–20 nm, length: 10–50 μm

-- Price: 2000 US$/kg





➢ Carbon Black (CB)

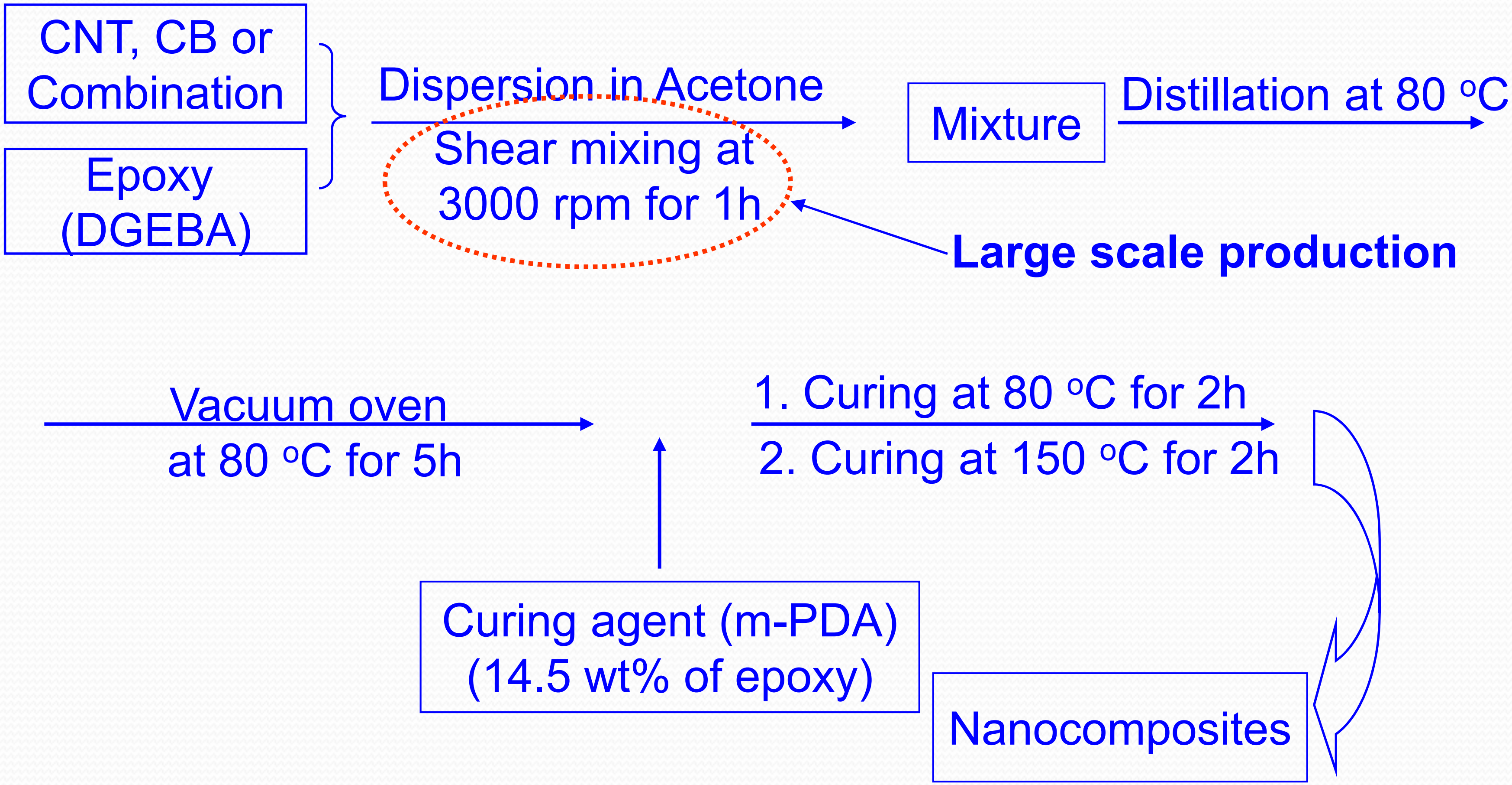
-- VULCAN XC72 (Cabot Corp.)

-- Diameter: 20-60 nm

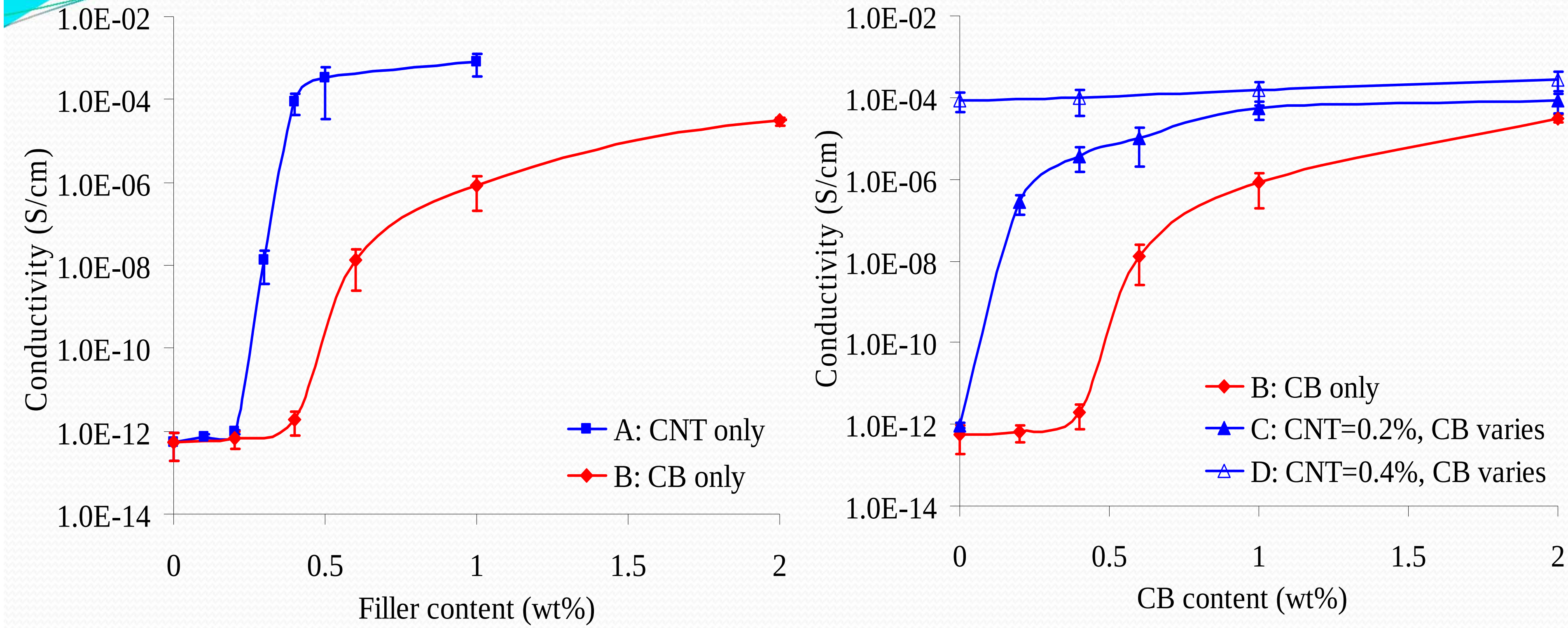
-- Major features: Excellent conductivity, good processability, etc.

-- Price: 30 US$/kg

Nanocomposite Fabrication

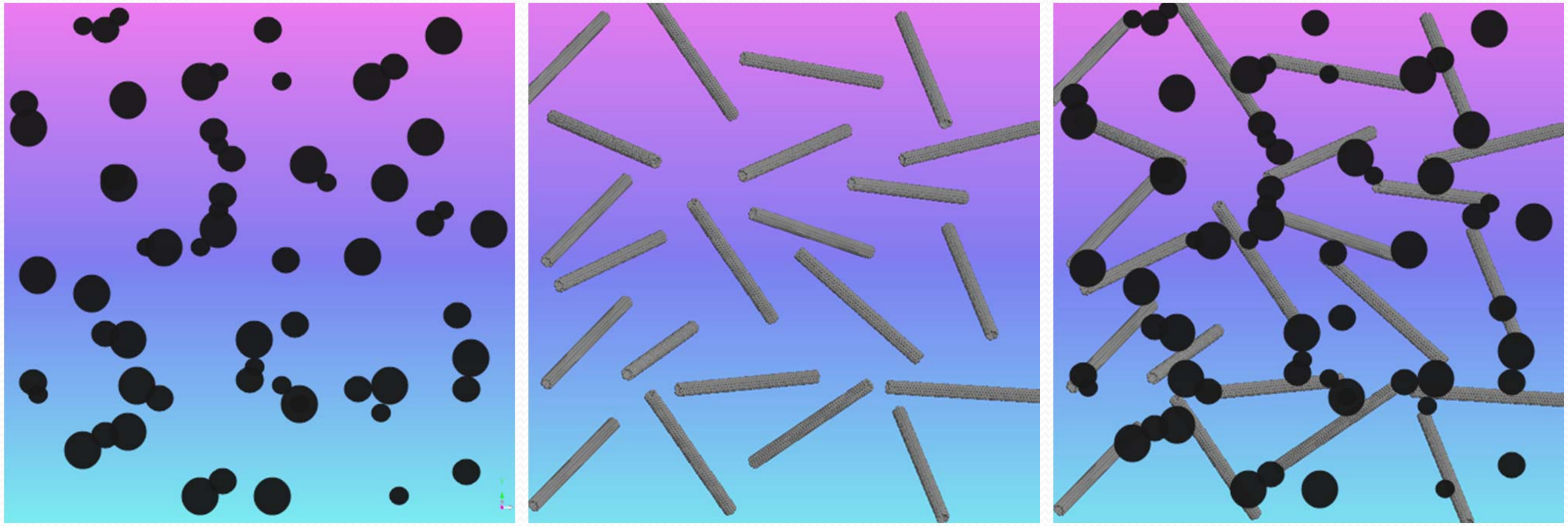


DC Conductivity of Nanocomposites



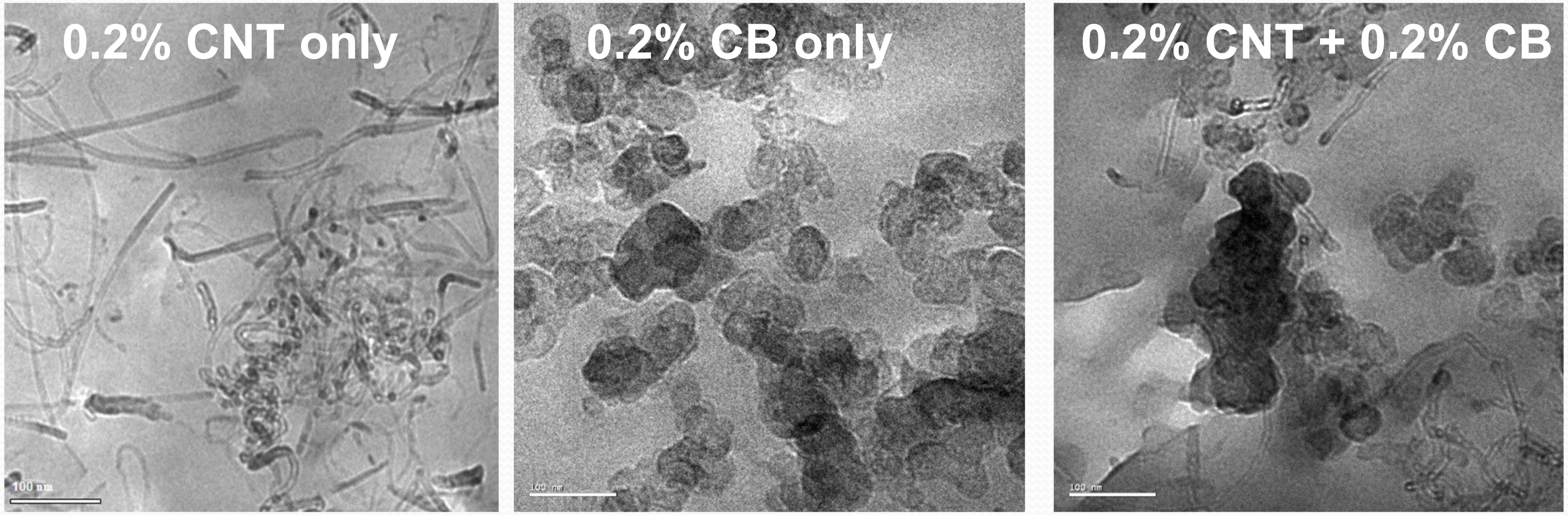
- Pc of nanocomposites:
  -- CNT: 0.3%; -- CB: 0.6%; -- Hybrid fillers: 0.2% CNT+0.2% CB
- CNT = 0.20 wt%: Significant increase with additional 0.20 wt% CB.
  -- Synergy between CNT and CB to form conducting networks
- CNT = 0.40 wt% (Above Pc): A marginal positive effect on electrical conductivity improvement due to the saturation of conducting networks.

Conducting Networks in Nanocomposites Containing Hybrid Fillers



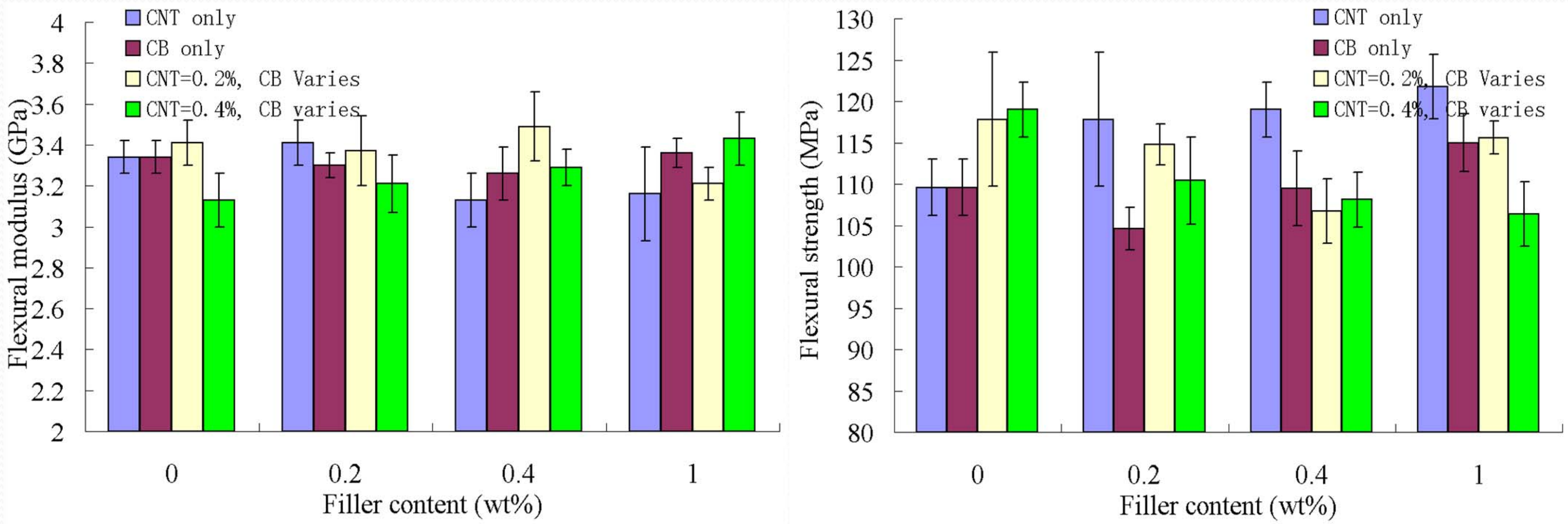
- Nanocomposites containing CB or CNT only (Figs. A & B), random dispersion of fillers, no formation of conducting networks in composites.
- Nanocomposites containing CNT and CB (Fig. C), formation of conducting networks.

Distribution of Conducting Fillers in Nanocomposites



- ➢ **CNT only** (Fig. A), large CNT agglomerates, no obvious conducting pathways;
- ➢ **CB only** (Fig. B), better dispersion, chain-like agglomerations;
- ➢ **Hybrid fillers** (Fig. C), CNTs were linked by CB, resulting in the formation of tight conducting networks.

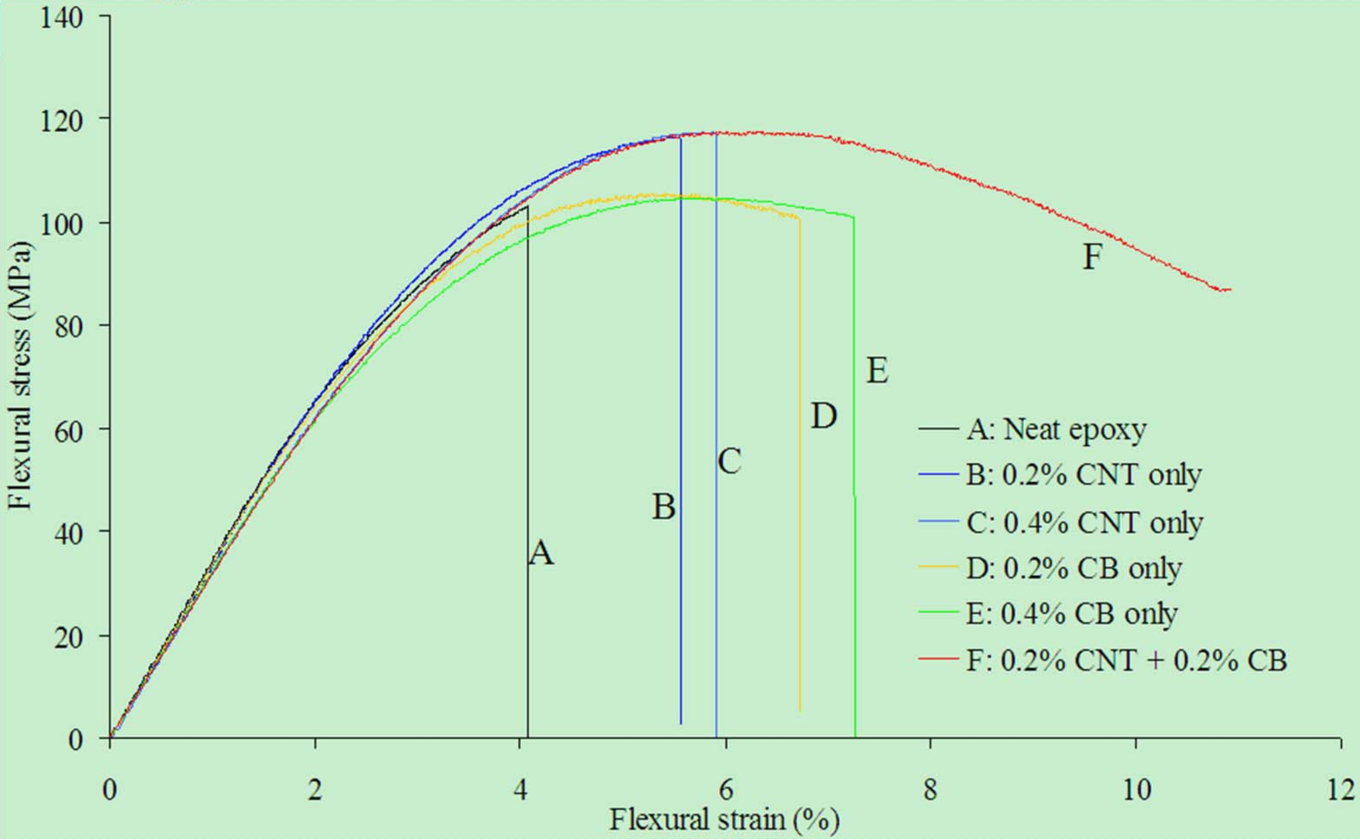
Mechanical Properties of Nanocomposites

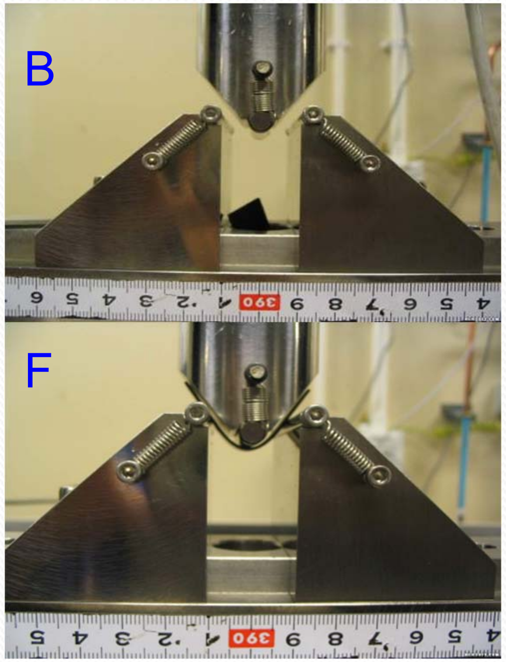


➢ No drastic changes on flexural properties of composites due to varying CNT and CB contents: Flexural modulus ~3.30 GPa, flexural strength ~ 1 10 MPa

➢ Relatively low modulus and strength due to no deliberate functionalizati on of CNTs for high electrical conductivity

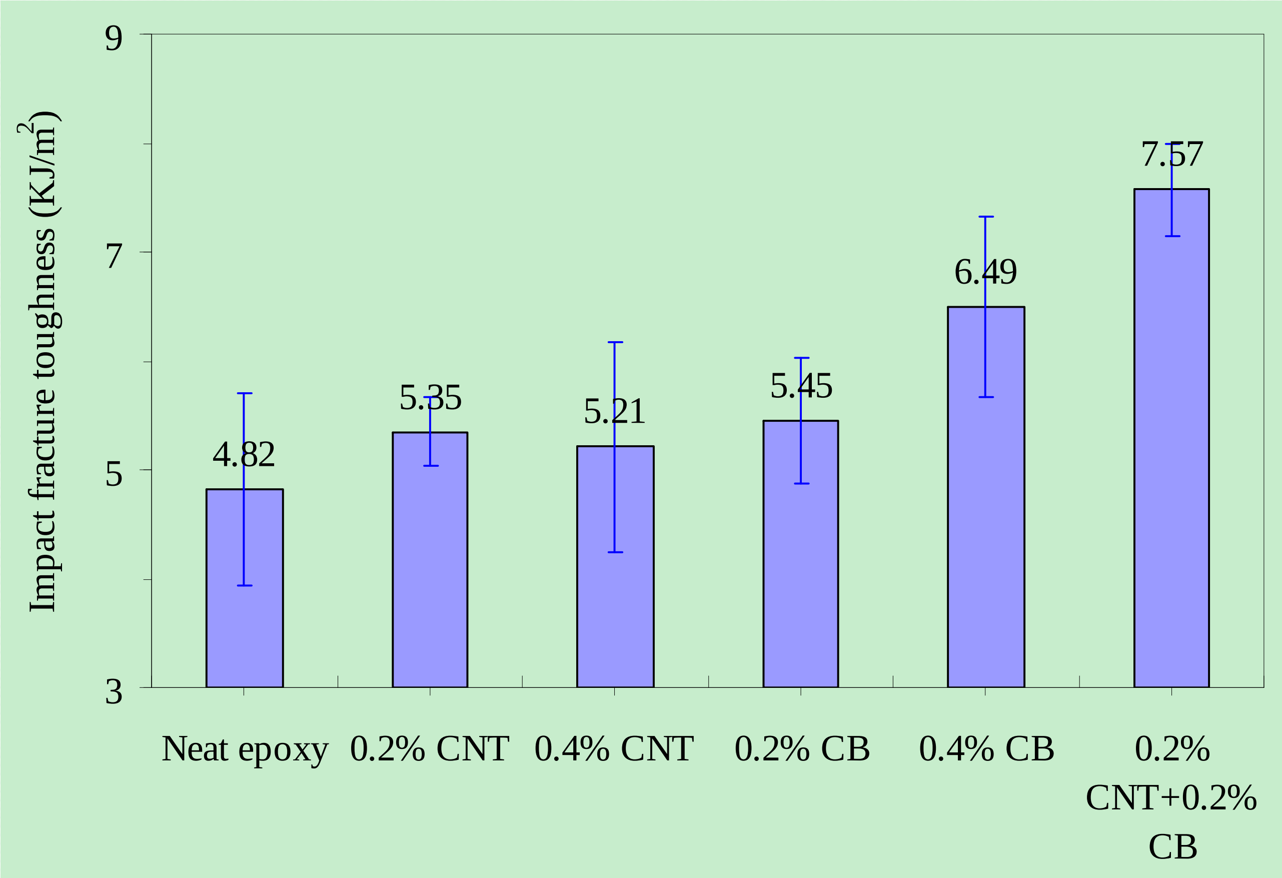
Ductility of Nanocomposites





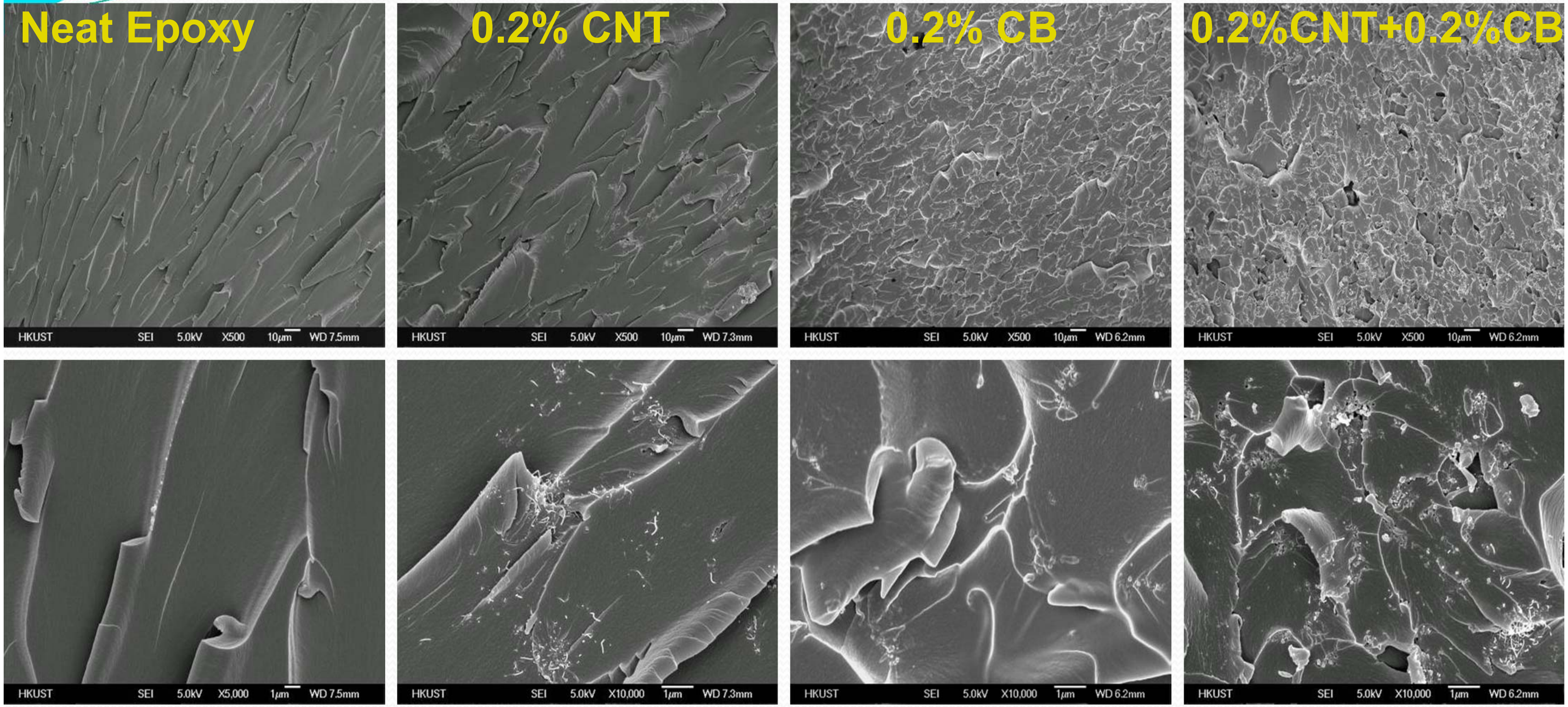
- ➢ Introduction of CB in epoxy, much larger deformation before fracture; More pronounced using hybrid fillers of CNT and CB
- ➢ CB played an important role in changing the fracture behavior of the nanocomposites from brittle to ductile failure.

Fracture Toughness of Nanocomposites



- > 50% (from 4.82 to 7.57 KJ/m^2) increase by incorporating hybrid fillers 0.2% each of CNT and CB particles
- Synergic effect of hybrid fillers in enhancing the fracture resistance of nanocomposites.

Fracture Morphologies of Nanocomposites



- ➢ Neat epoxy and 0.2% CNT nanocomposites: Typical ***brittle fracture***;
- ➢ CB nanocomposites: Irregular and smaller-sized ridges, ***more ductile***;
- ➢ ***Increased surface roughness with multi-direction features*** on a sub-microscopic scale: Responsible for the enhanced ductility and fracture toughness

Summary

- Development of epoxy-based nanocomposites containing hybrid fillers of CNT and CB
- Evaluation on the electrical and mechanical properties of the composites
- Hybrid fillers of CB and CNTs: Enhanced electrical conductivity of the nanocomposites. A low percolation threshold with with 0.20 wt% CNTs and 0.20 wt% of CB.
- Synergic effect using hybrid fillers:

  -- Improved ductility and toughness of nanocomposites

  -- Maintained high modulus(~3.30 GPa) and strength (~110 MPa).

Concluding Remarks

Applicable to other Nanoparticles

- **Fundamental: Dispersion and functionalization**

  -- CNT functionalization using silane: Improved dispersion and interfacial interaction between CNTs and epoxy matrix.

  -- CNT functionalization using ball milling: A simple and cost effective method for introducing functional groups on CNTs.

  -- Functional groups on CNTs: Governing factors for the mechanical and electrical properties of CNT/polymer composites.

- **Application**

  -- Structural composites: Improved mechanical properties of CNT/polymer nanocomposites

  -- Functional composites

  ✓ Ag@CNTs: Higher electrical & thermal properties, remained mechanical properties

  ✓ CNT-CB hybrid fillers: Lower Pc and cost, improved ductility and toughness.

  ✓ New materials to prepare multi-functional composites

Polymer-based Nanocomposites with Multi-functional Properties

Carbon-based Materials

Ore deposits, used 4000 B.C.

Lamp smoke, used as black pigment in ~ 300 BC

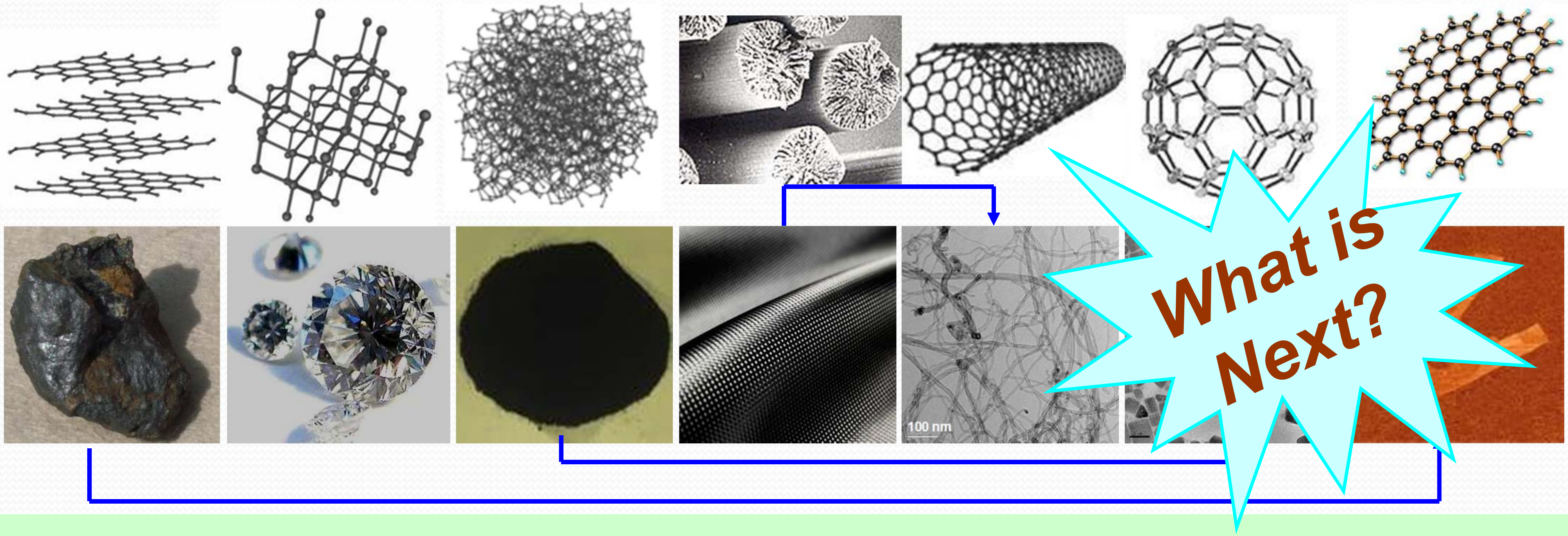
1879, filaments for light bulbs; ~ 1950s, FRP application

~ 1950s, CF research

1991, observation using TEM

Study on interstellar dust & graphite, 1985

Mechanical cleavage, 2004



Black Material, Bright Future

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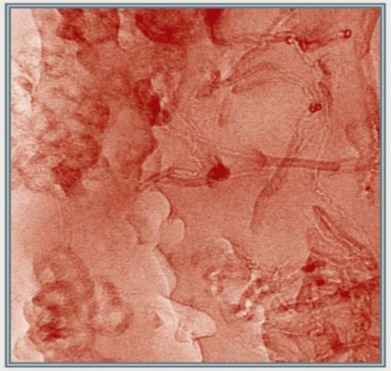
CARBON NANOTUBES FOR POLYMER REINFORCEMENT



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