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Carbon nanotubes and graphene nanoplatelets for multi-functional composites

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Outline

1. Brief introduction to carbon nanotubes (CNTs) and graphene nanoplatelet
2. Single walled carbon nanotubes (SWNTs)- Nylon 6 composite fiber
3. Graphene-epoxy composite
4. CNTs/carbon fiber 3D matrix composite
5. Work @ Sabic Innovative Plastics
6. Work @ UW

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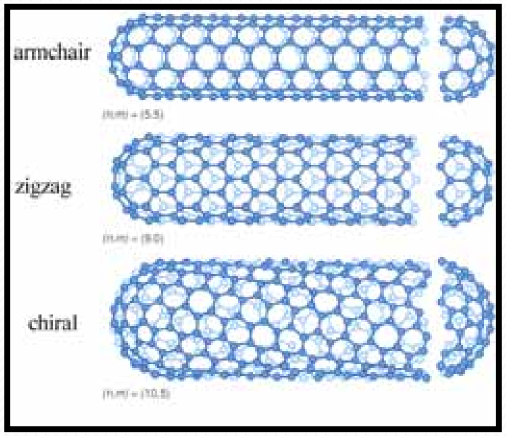
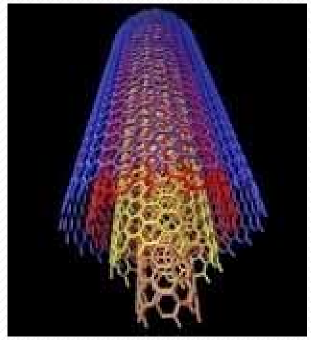
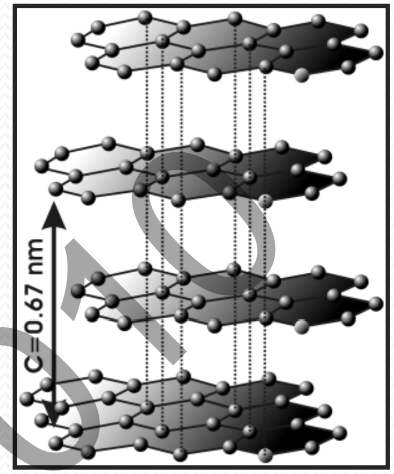
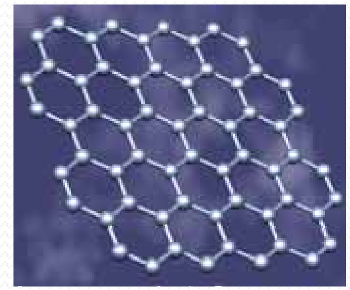
Carbon nanotube & graphene nanoplatelet





1991-1993

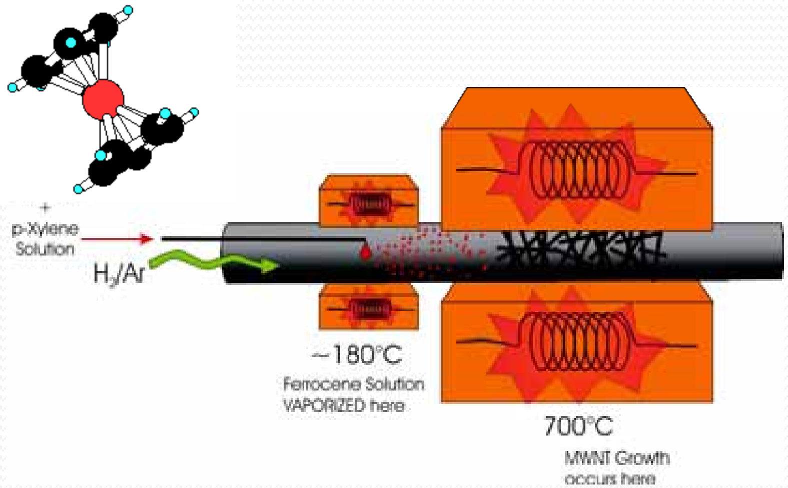


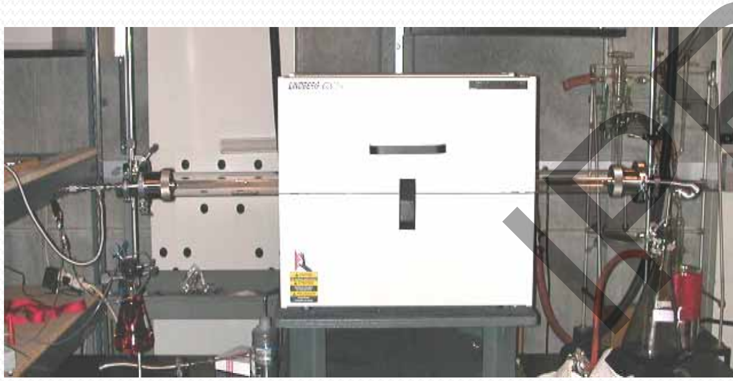


2002-2005

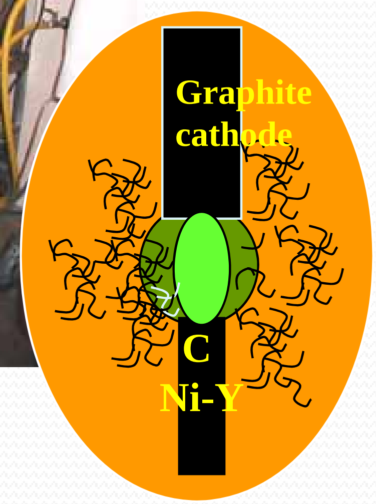
- High mechanical strength and tensile modulus
  (Young's modulus ~1TPa, carbon fiber: 400-600 MPa
- Unique electrical properties (~1*10^5 S/cm)
- Exceptional thermal conductivity (~3000 W/mK)
- low density(~1.3-2g/ml) high aspect ratio (L/D~1000)

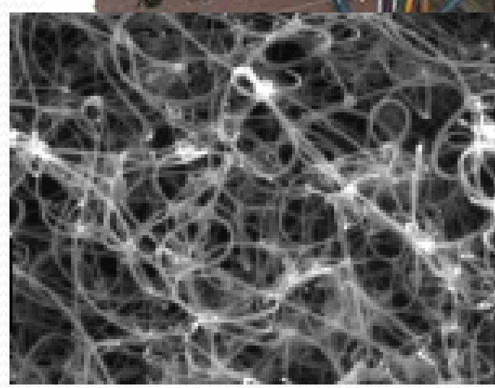
Synthesis of carbon nanotubes





Chemical vapor deposition





Arc-discharge

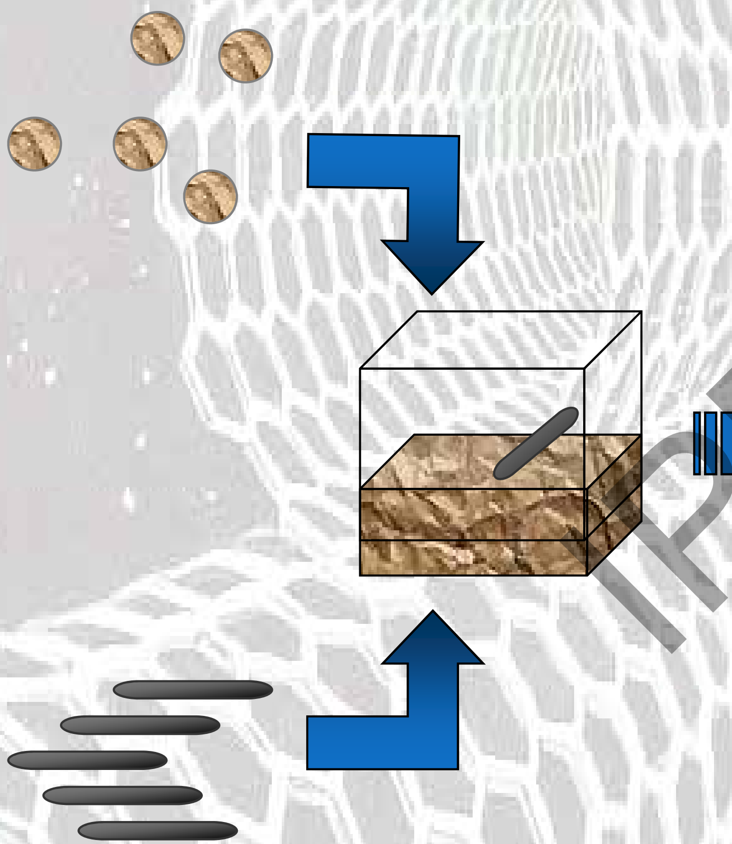
Applying SWNTs & GNPs to polymers

High mechanical properties

Antistatic

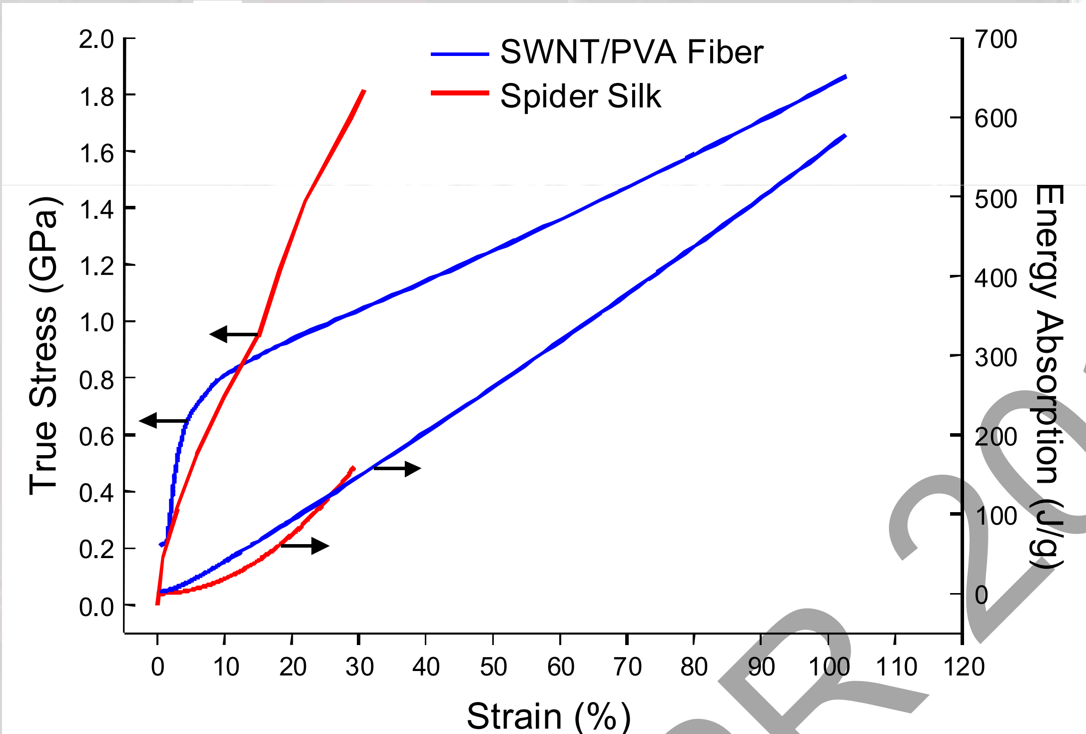
EMI shielding

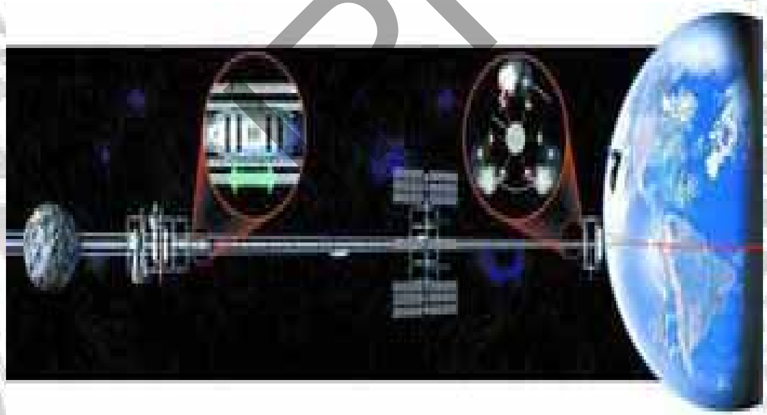
Against lighting strike



Nano-materials will bring revolution to industry

Brief example-strongest polymer composite ever made





Tensile strength matches spider silk and modulus (80 GPa) is much higher than spider silk

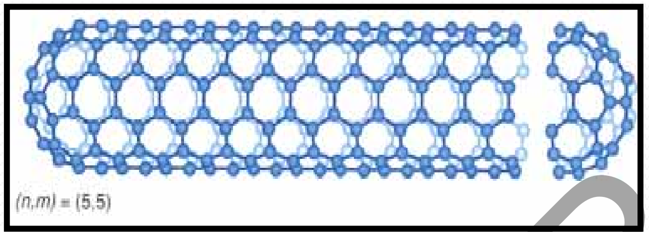
R. Baughman, 290,1310, Science, 2000

Nylon 6/SWNT Advanced Composites --- mechanical/electrical enhancement

Yu,A. et at., J. of American Chemical Society 2005, 127

Motivation and challenges

- Nylon is a widely used thermoplastics owing to its good strength high elongation, excellent abrasion resistance, etc
- There is need to improve the mechanical strength, toughness and electrical conductivity.



Highly hydrophobic surface

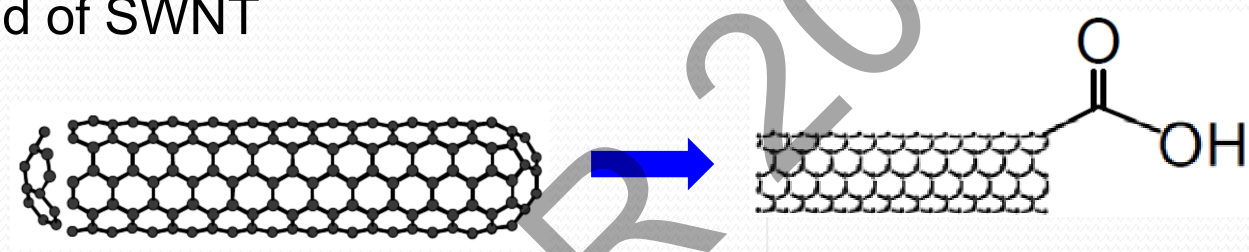
- Lack of functionality resulting chemical incompatibility with the polymer matrix and the self-aggregation of SWNTs into bundles due to van der Waals attraction

- Homogeneous dispersion & SWNTs not pull out from polymer

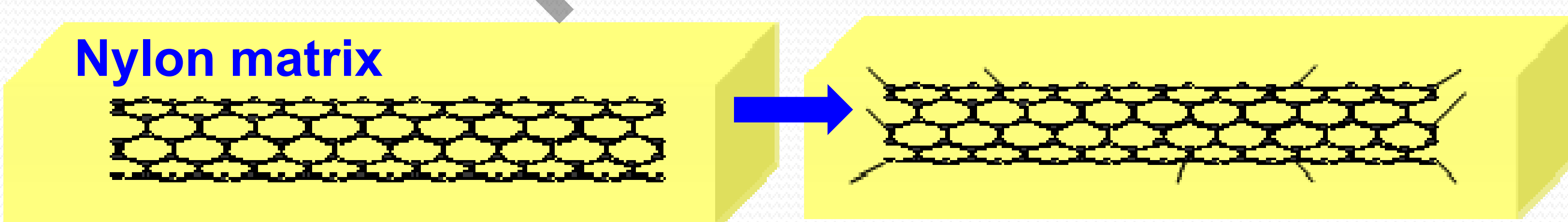
Strategy

Ensure efficient load transfer from the matrix to the fiber, the interfacial bonding between the polymer matrix and the carbon nanotubes is necessary to prevent fiber pull out

Controlled HNO_3 treatment of SWNTs, brings –COOH to the end of SWNT

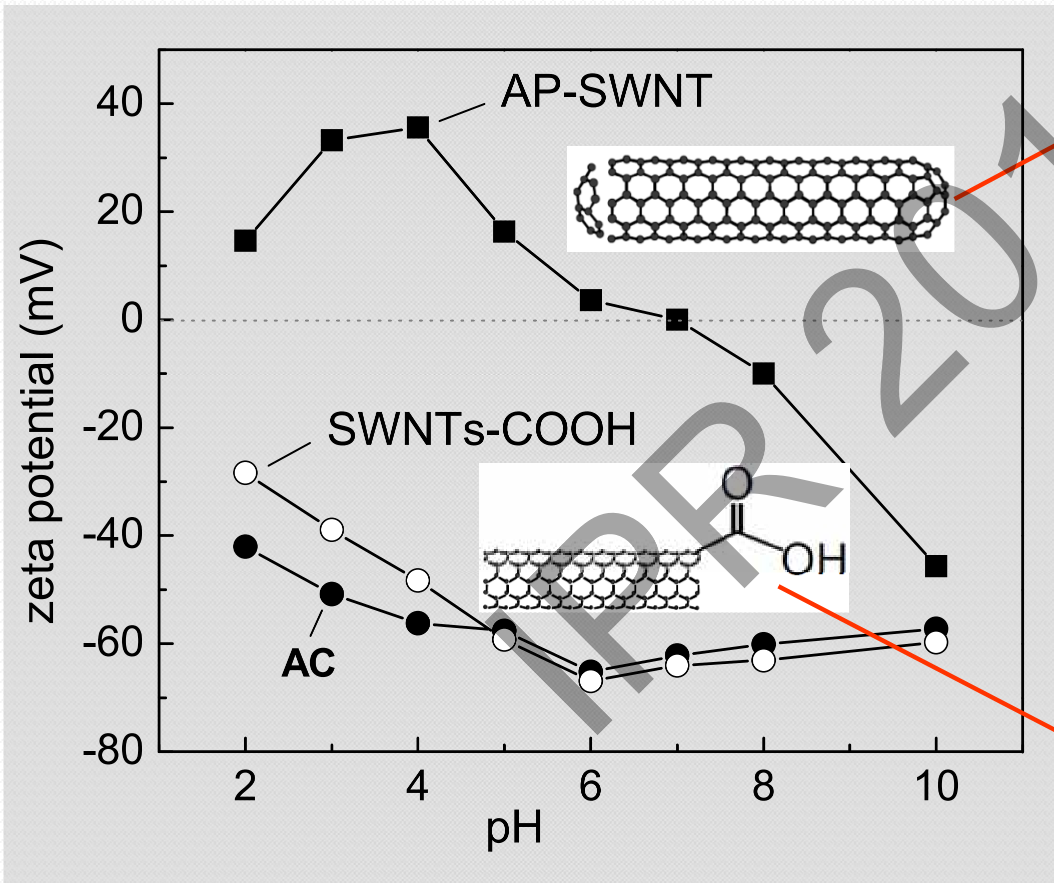


In-situ grafting PA6 chain to SWNT surface



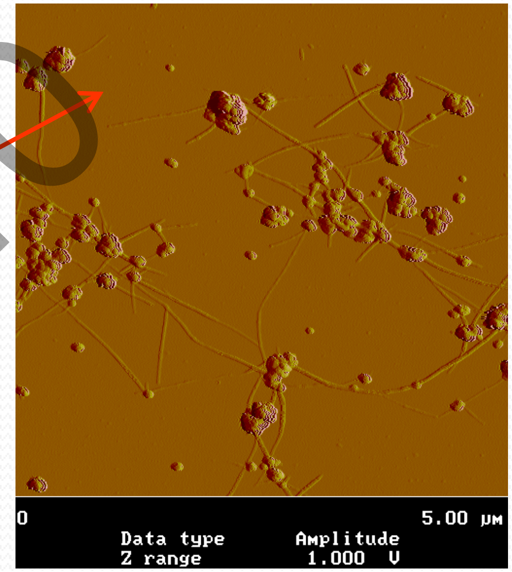
Step one: HNO_3 treatment

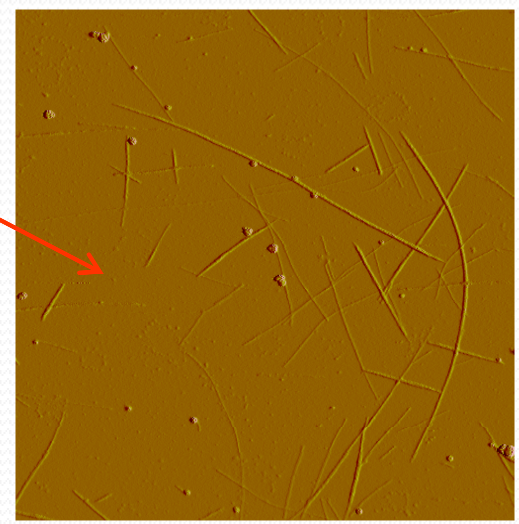
1. SWNT surface hydrophilic



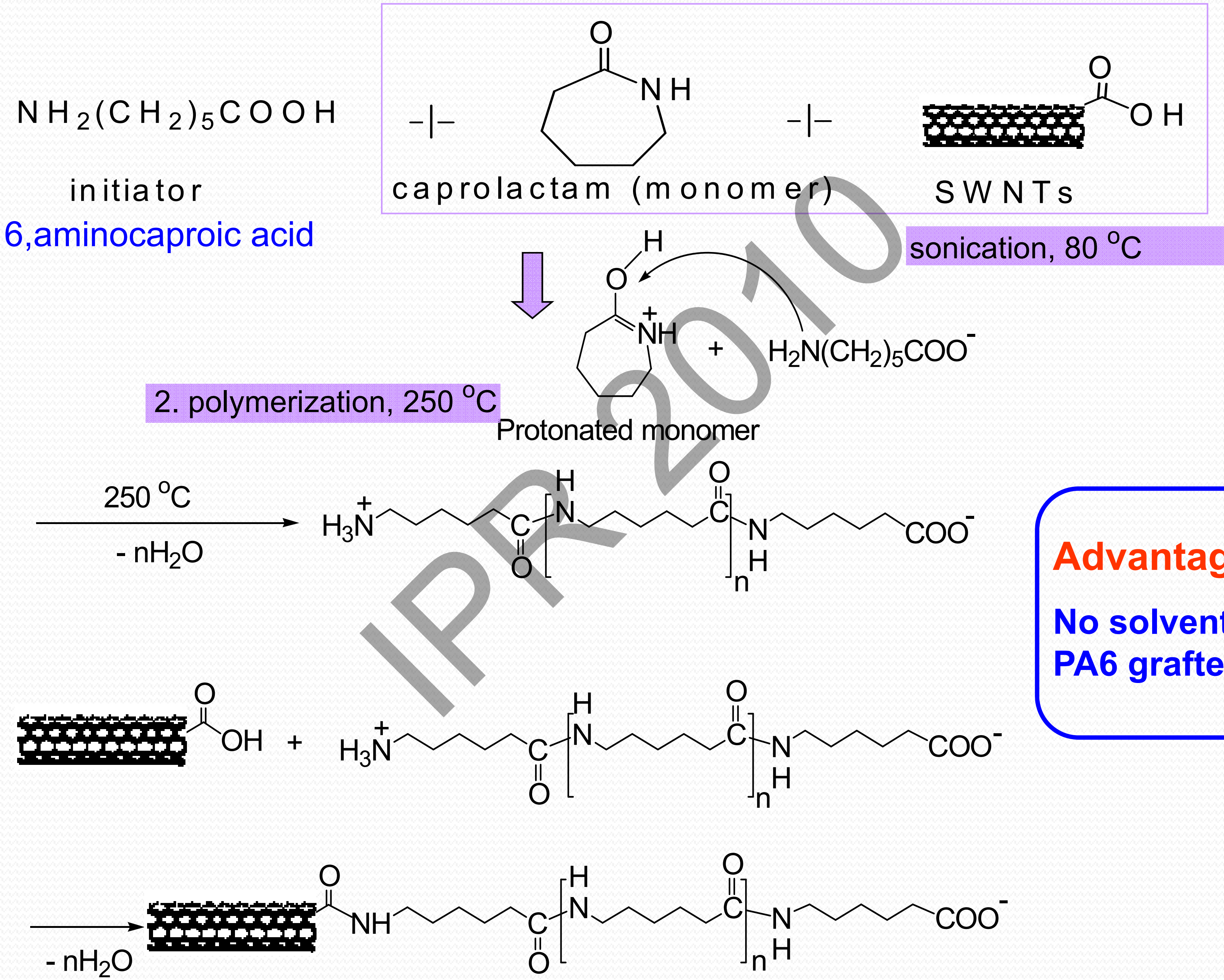
2. Removed catalyst particles

Atomic Force Microscopy





Step 2: In-situ grafting nylon 6 to SWNT



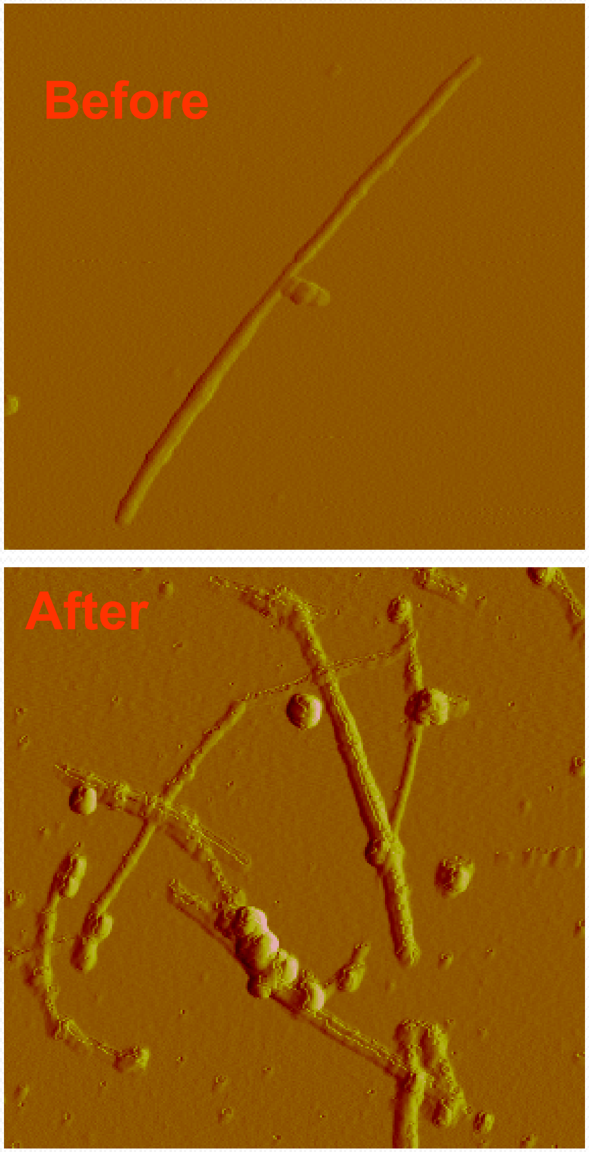
Advantages:

No solvent

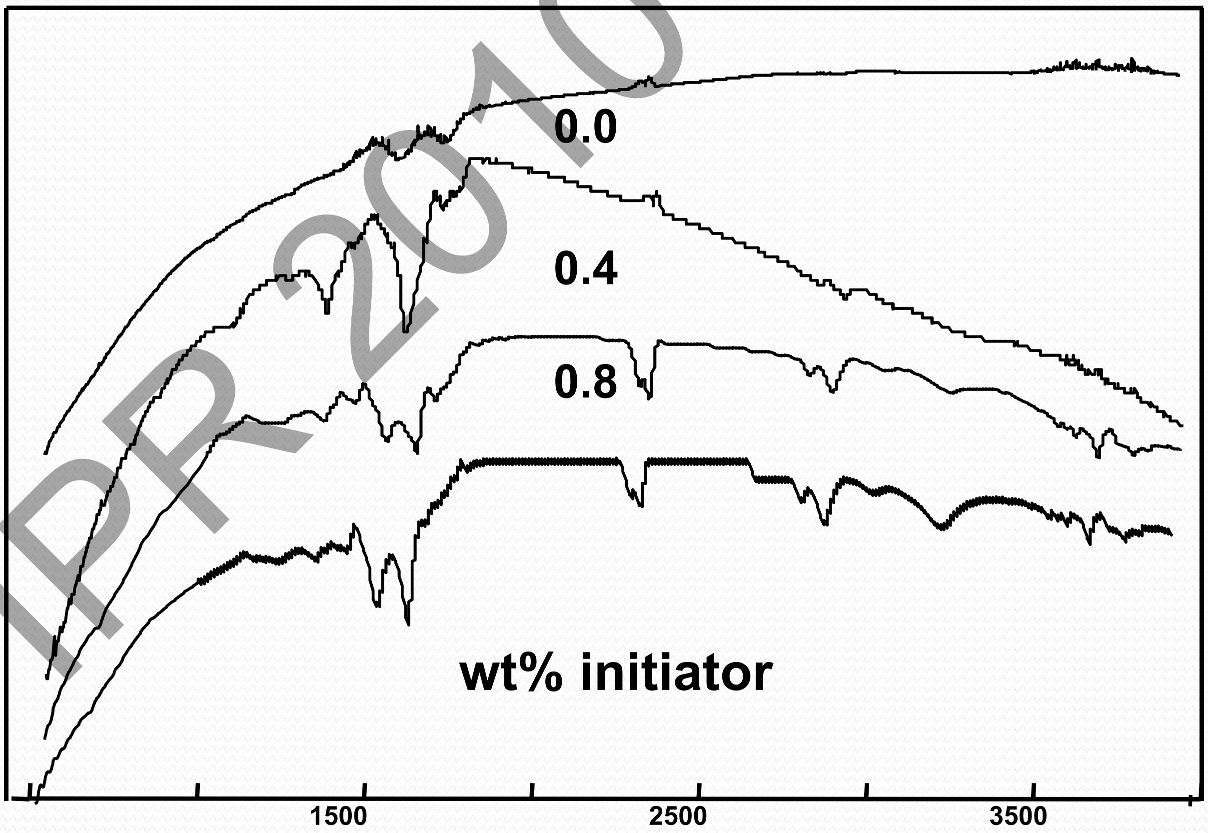
PA6 grafted to SWNT

Characterization of SWNTs with grafted Nylon 6

AFM of SWNT



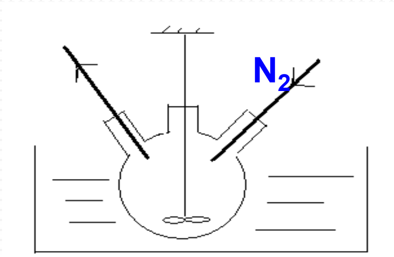
IR spectra samples prepared using different initiator concentrations

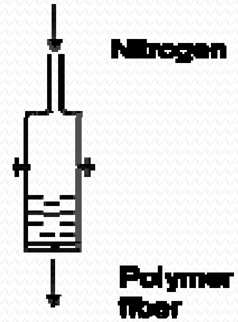


1640 cm^{-1} → C=O group of the amide functionality

1540 cm^{-1} combination of N-H bond C-N bond of the amide group

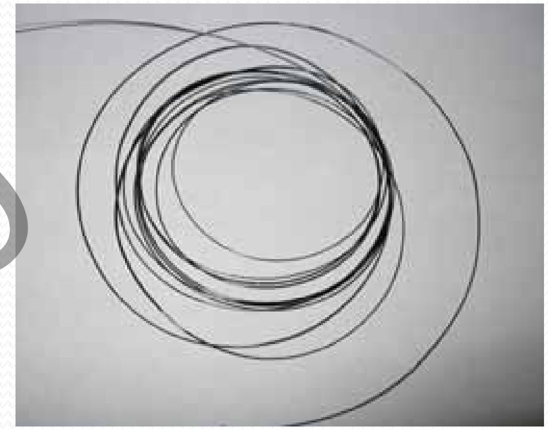
In situ polymerization setup & fiber preparation



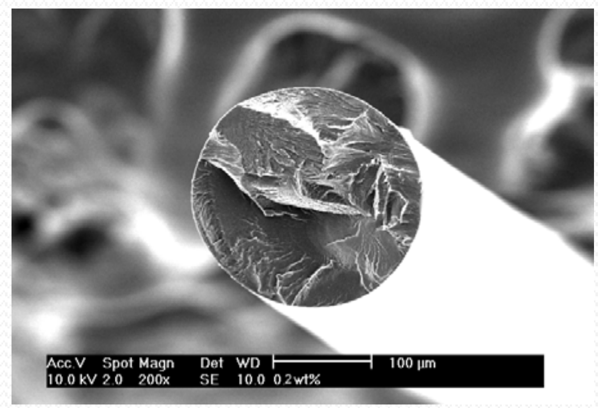


Lab reactor

fiber spinneret

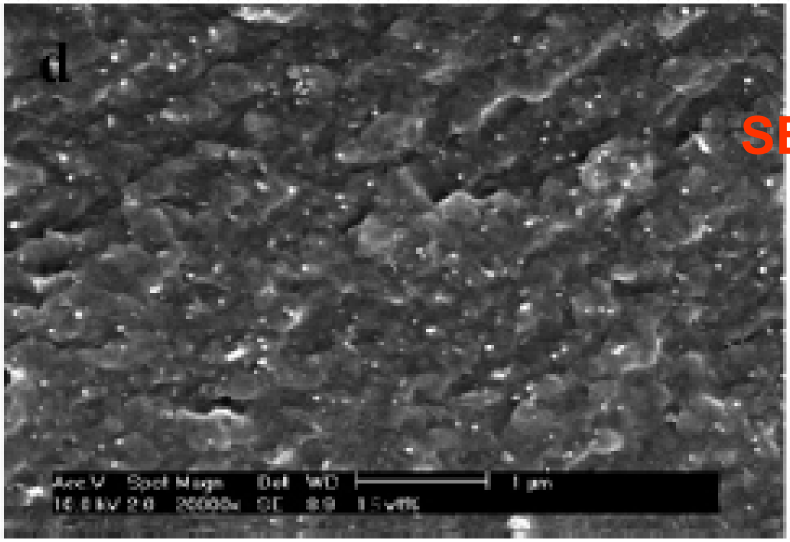


Composite fibers

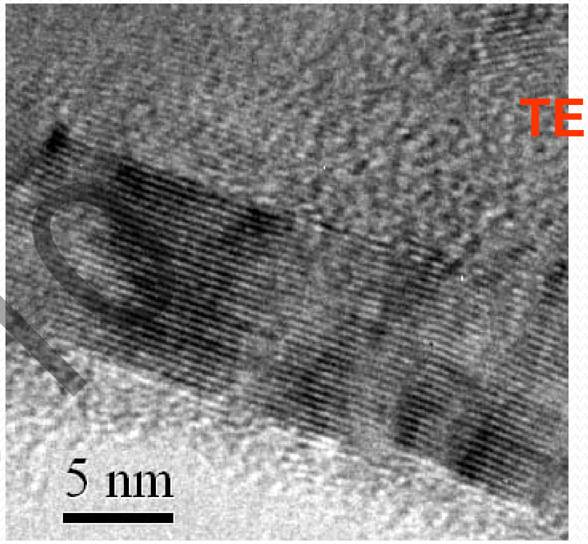


Cross-section

Characterization of SWNTs-Nylon 6 composite

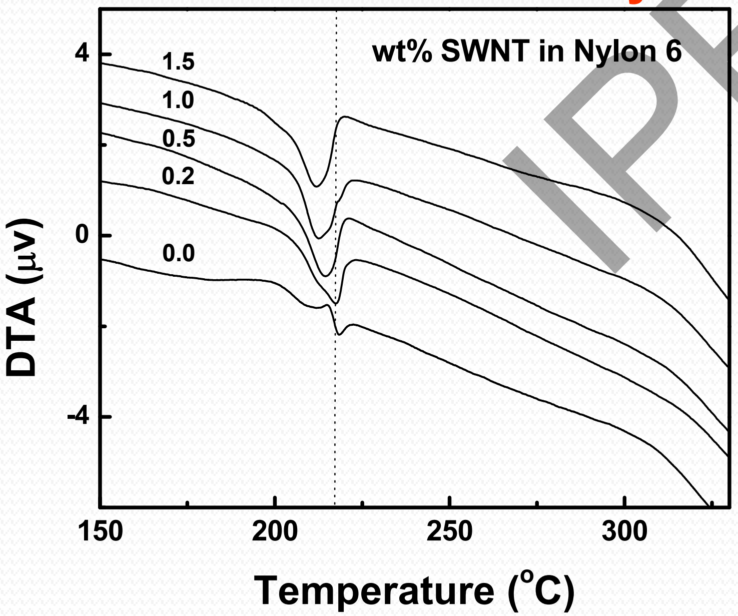


SEM

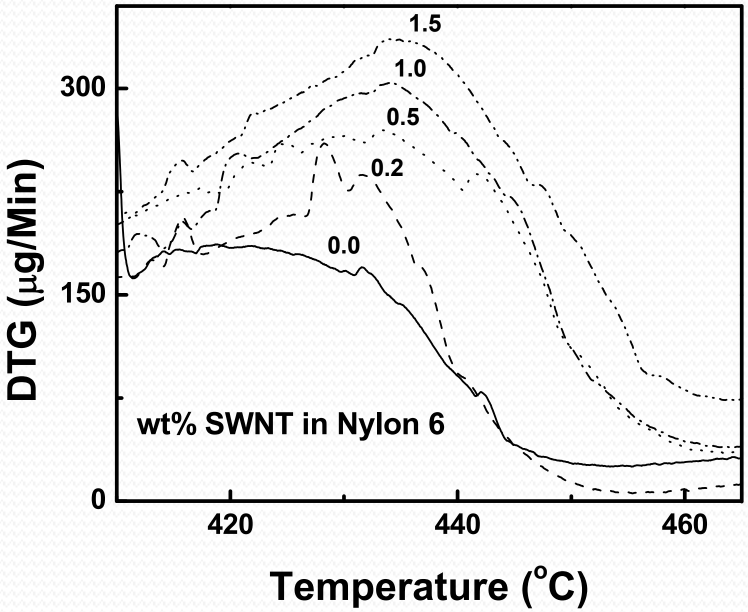


TEM

Differential thermal analysis.



Thermal decomposition T.

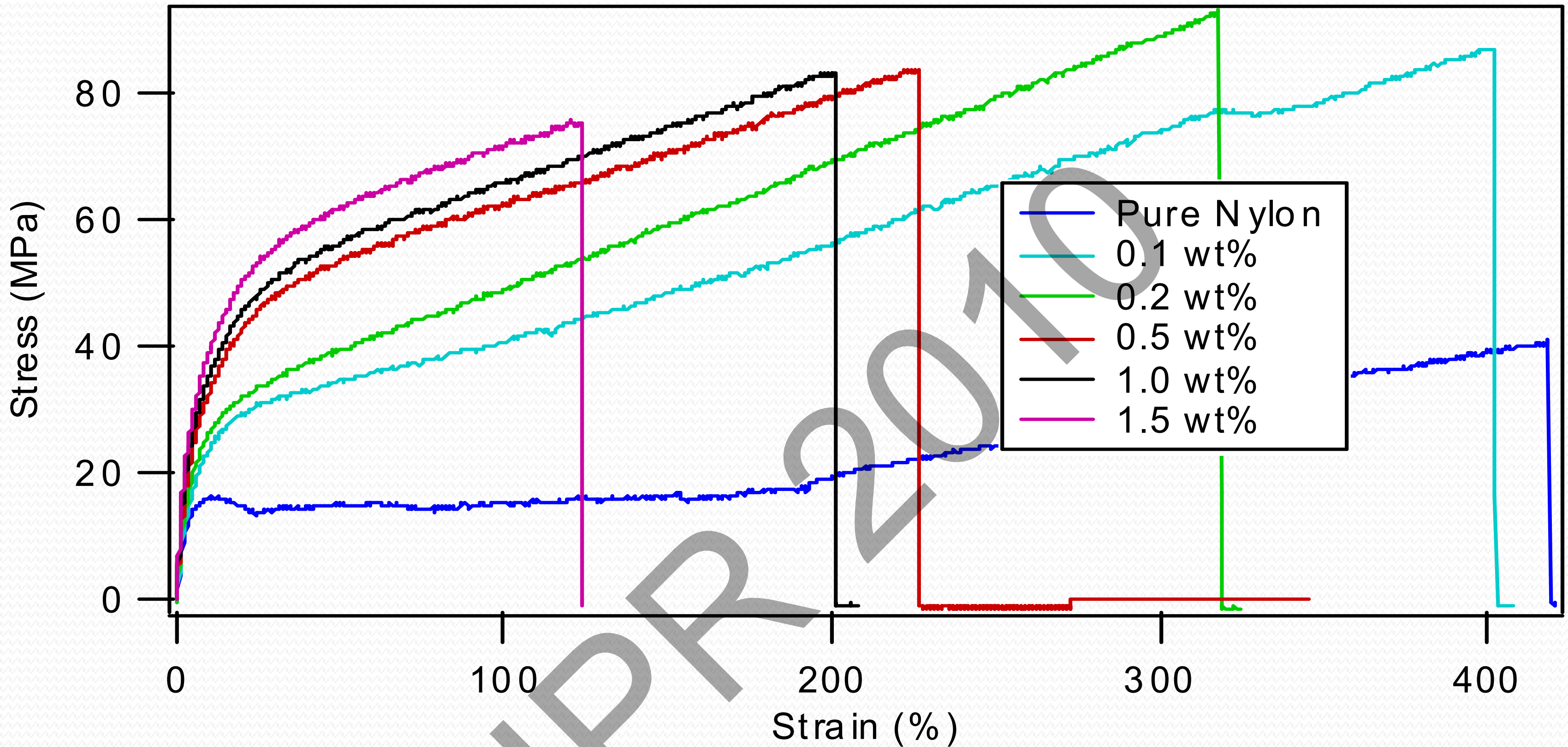


Results of electrical conductivity

Samples @ 1wt % loading	Electrical conductivity (S/cm)
PA6 grafted SWNT composite	1.1E-6

Electrical conductivity data show:
The composites are in the anti-static range
1 wt % SWNT loading

Mechanical properties of SWNTs-Nylon 6 composite



	pure nylon	0.1 wt % SWNTs	0.2 wt % SWNTs	0.5 wt % SWNTs	1.0 wt % SWNTs	1.5 wt % SWNTs
tensile strength (MPa)	40.9	86.0	92.7	83.4	83.0	75.1
Young's modulus (MPa)	440	540	657	840	1115	1200

The PA6 grafted leads to 84 % increased tensile strength and 170% Young's modulus (1.5 wt% loading)

Modeling calculation of SWNTs-Nylon 6 composite

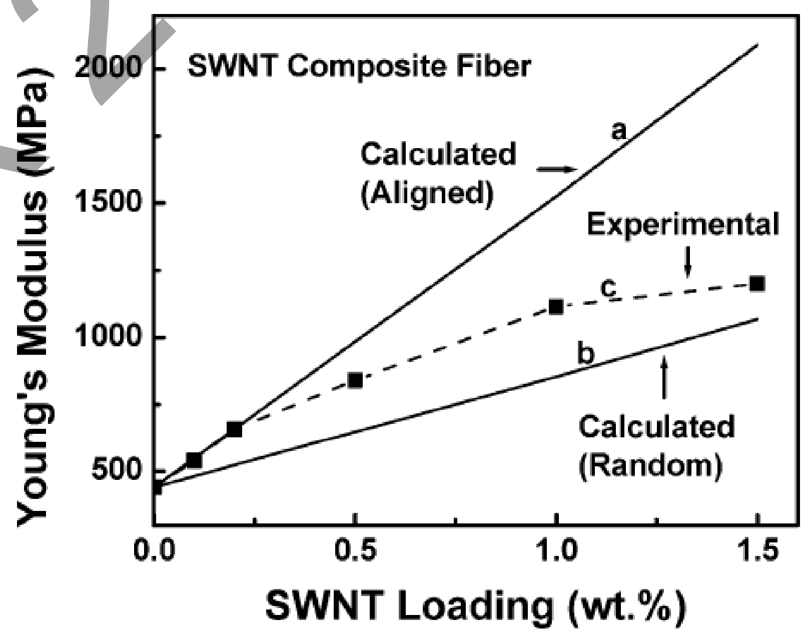
Halpin–Tsai model

Is widely used to predict the modulus of unidirectional or randomly distributed filler-reinforced composites

$$E_c = \left[\frac{3}{8} \frac{1+2(l_{NT}/d_{NT})\eta_L V_{NT}}{1-\eta_L V_{NT}} + \frac{5}{8} \frac{1+2\eta_\perp V_{NT}}{1-2\eta_\perp V_{NT}} \right] E_m$$

$$\eta_L = \frac{(E_{NT}/E_m)-1}{(E_{NT}/E_m)+2(l_{NT}/d_{NT})}$$

$$\eta_\perp = \frac{(E_{NT}/E_m)-1}{(E_{NT}/E_m)+2}$$



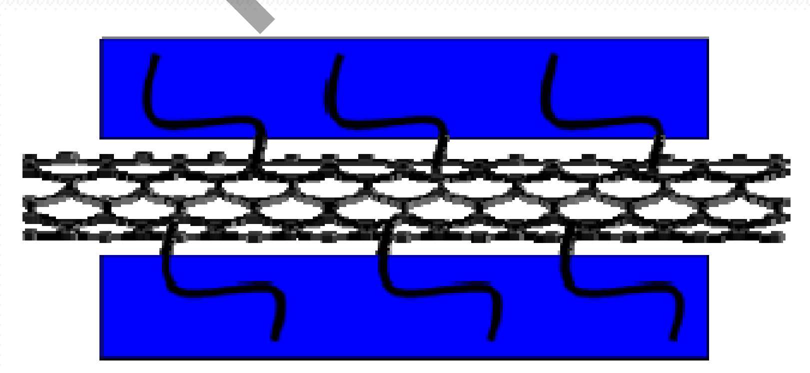
Summary

❖ The PA6 chains are found to be grafted to the SWNTs by a condensation reaction between the –COOH groups of the SWNTs and the terminal amino group of PA6

❖ The grafted PA6 chains enhance the SWNT-nylon6 interfacial interaction and improve their compatibility, → a homogeneous dispersion of the SWNTs in the nylon matrix

❖ The Young's modulus, tensile strength, and thermal stability of nylon 6 fibers are greatly improved by the incorporation of SWNTs via the process

❖ The composite is also anti-static in the pursued concentration range

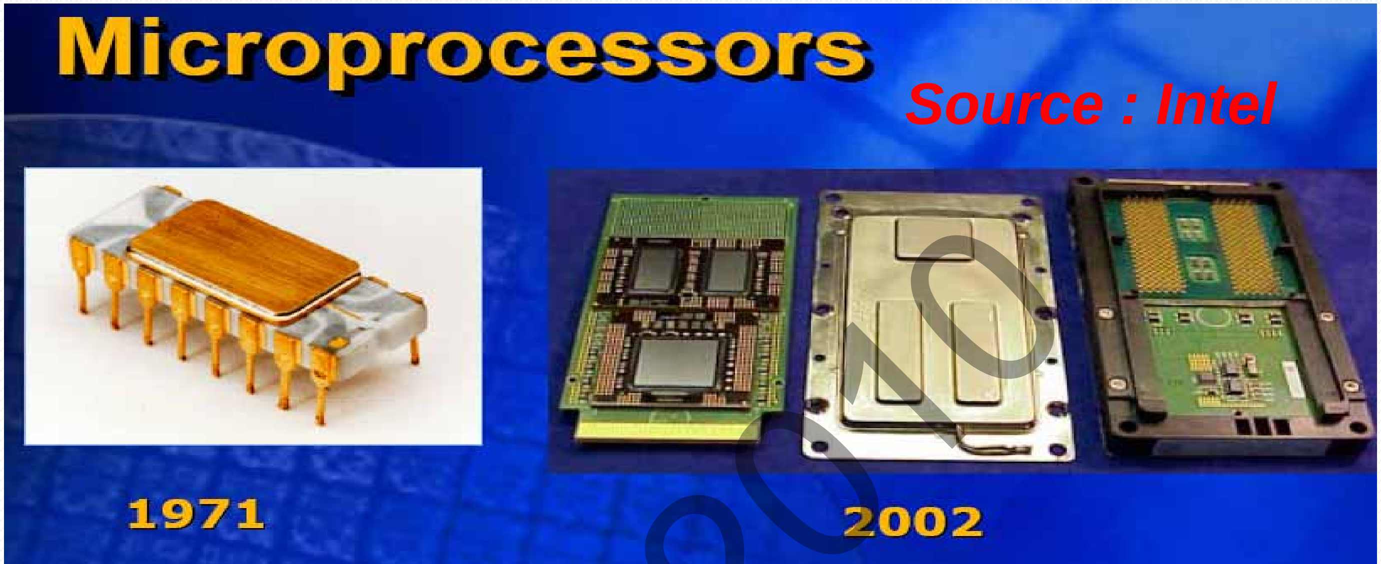


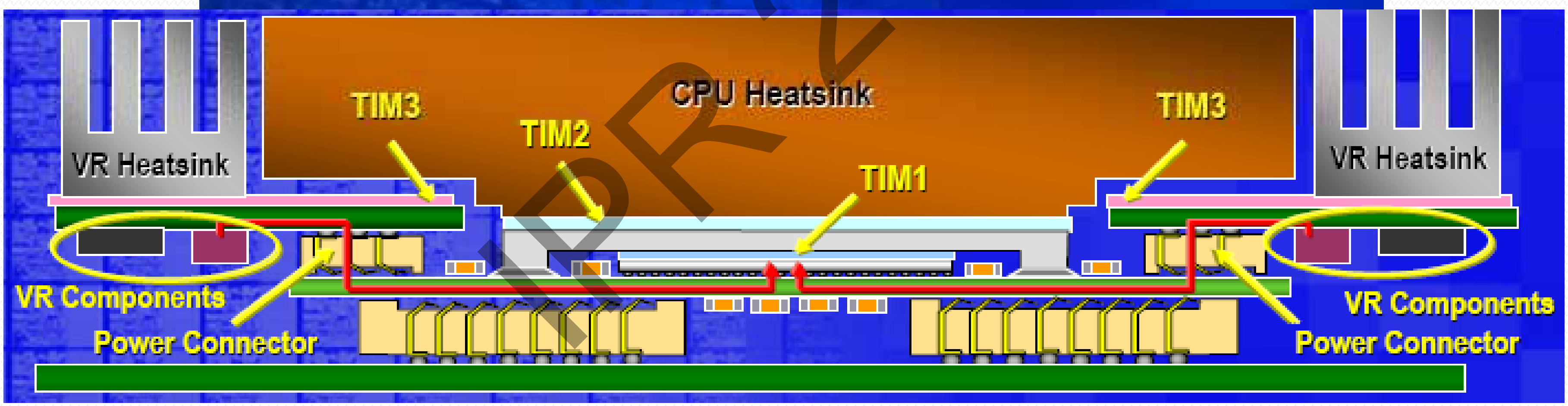
Graphene/ Epoxy Resin Composites
--- Thermal Interface Materials

Patent : US and WO patent: WO/2008/143692

Yu,A. ;Ramesh P. ;Itkis M.; Bekyarova E.; Haddon R., *J. of Physical Chemistry C* 2007,*111*,7565-7569

Composites: Thermal management in high density electronics





Thermal interface material (TIM)

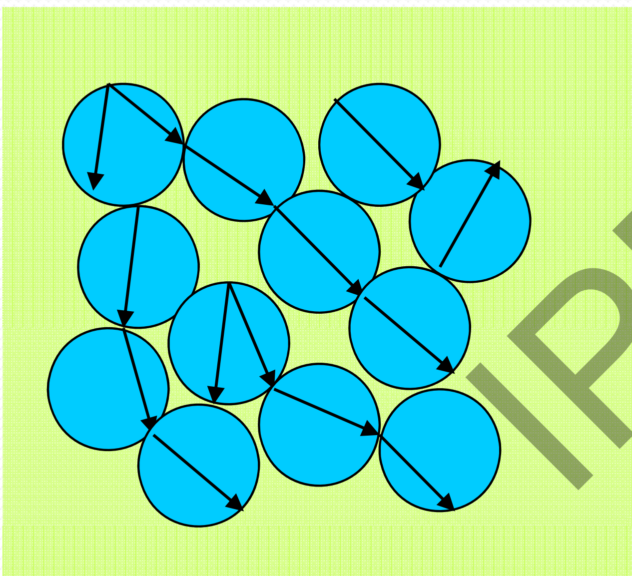
With continued scaling of devices, heat-transport problems will most likely be aggravated at all levels

GNPs as fillers in epoxy matrix for TIMs

Requirements of TIMs:
Thermal conductivity ≥ 2 W/mK
Low thermal expansion

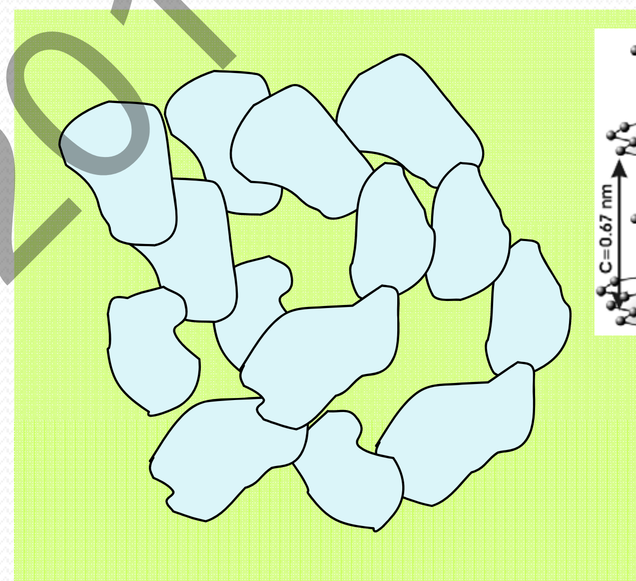
Thermal conductivity of polymer matrix: 0.2-0.4 W/mK

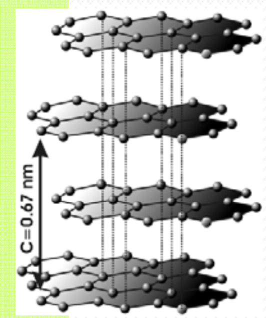
Conventional Particles:
SiO_2, AlN, Ag



Disdvantages:
Low aspect ratio
high loading

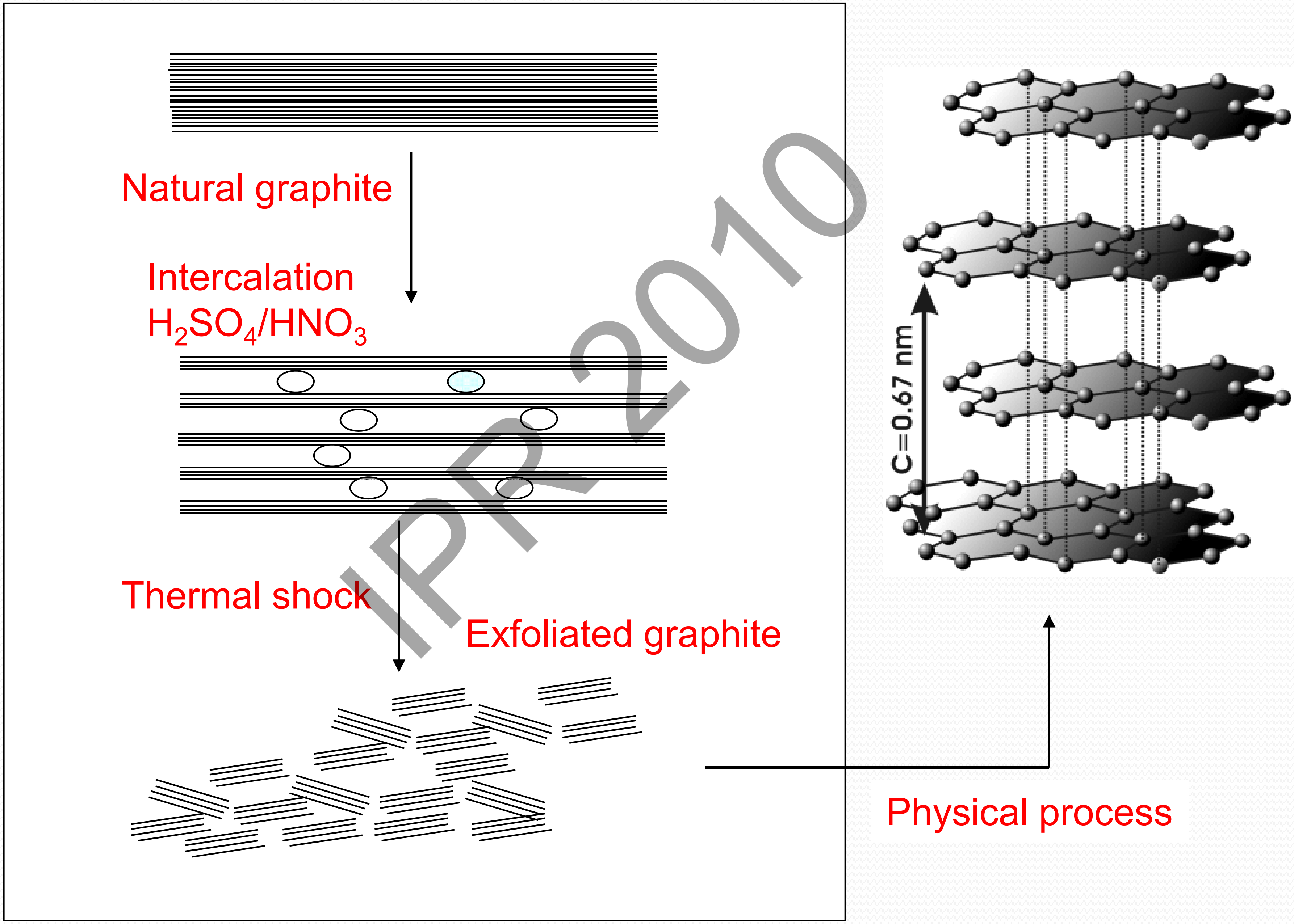
Using GNPs as filler





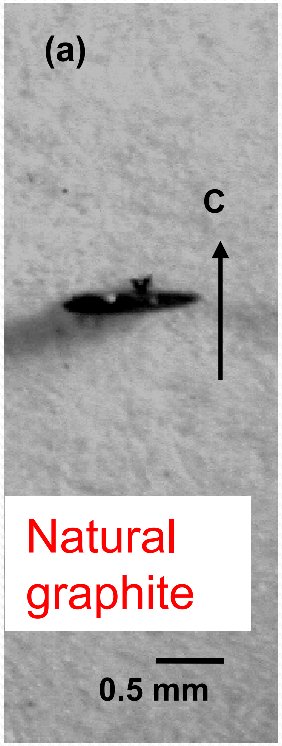
Advantages of GNPs
- High thermal conductivity
- High aspect ratio
- Low CTE
- Low density

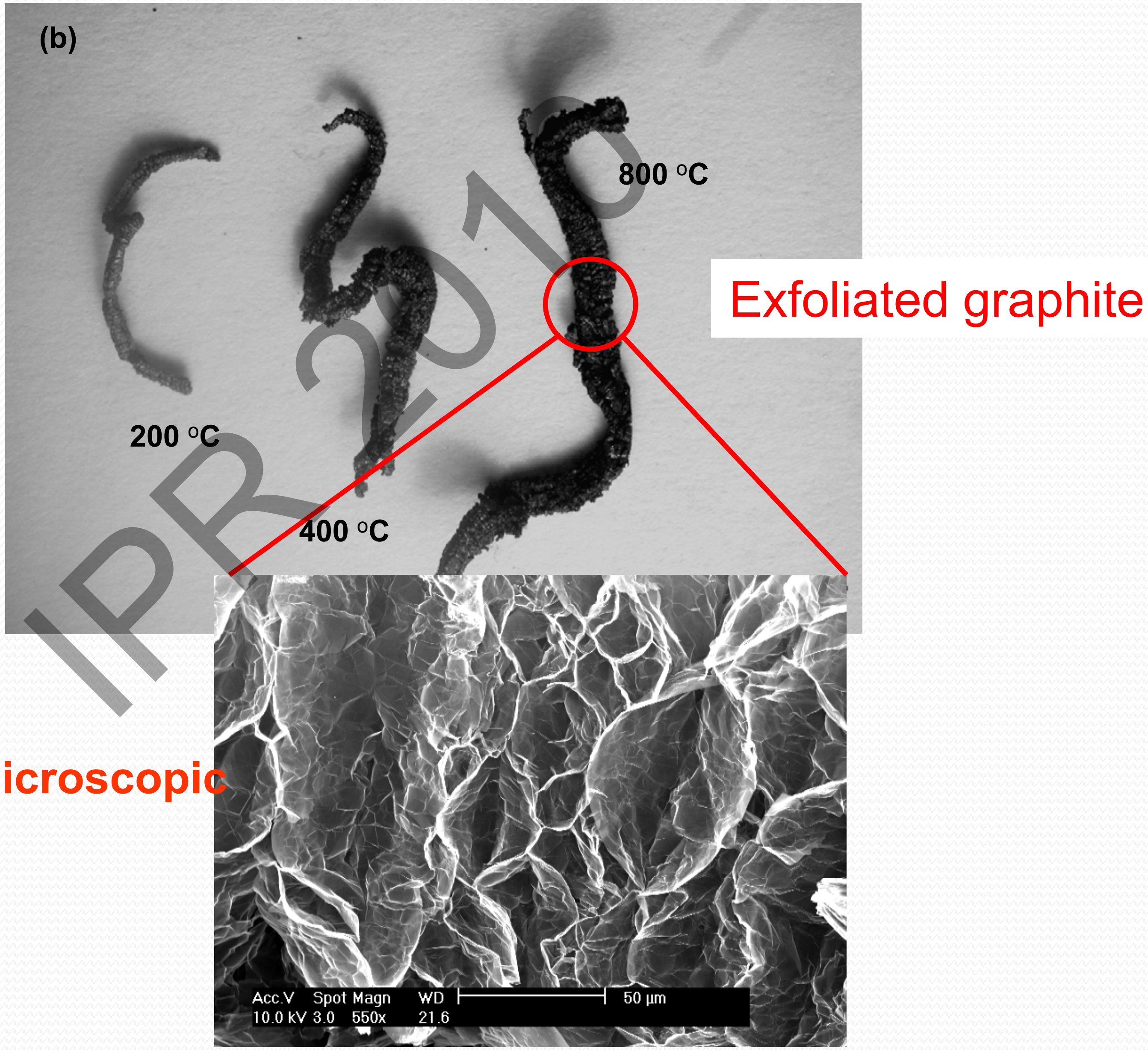
Schematic process to obtain GNPs



Microscopic observation of GNPs

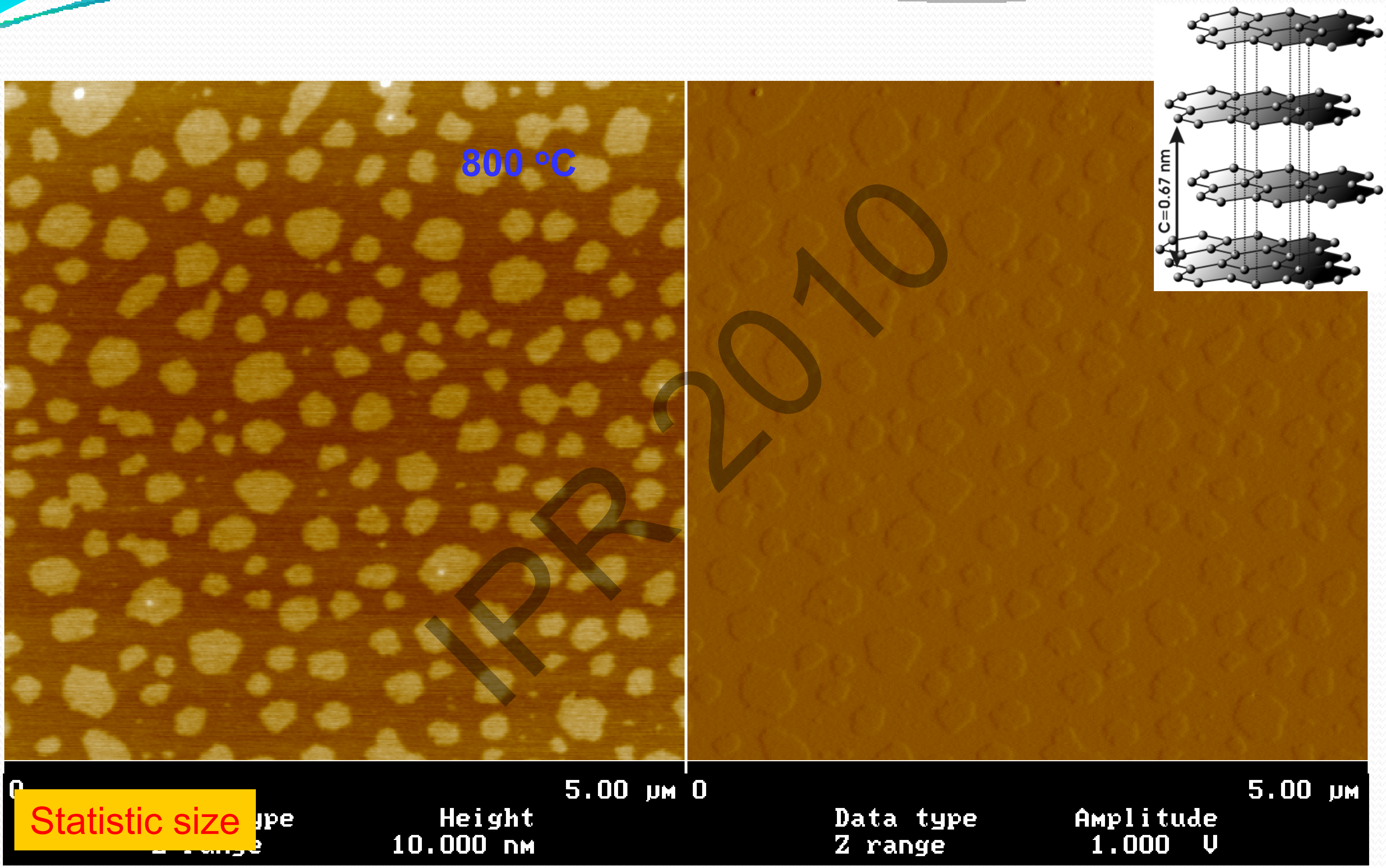
Optical Microscopic





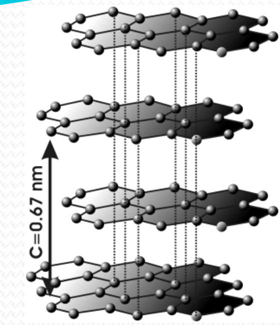
Scanning Electron Microscopic

AFM of GNPs



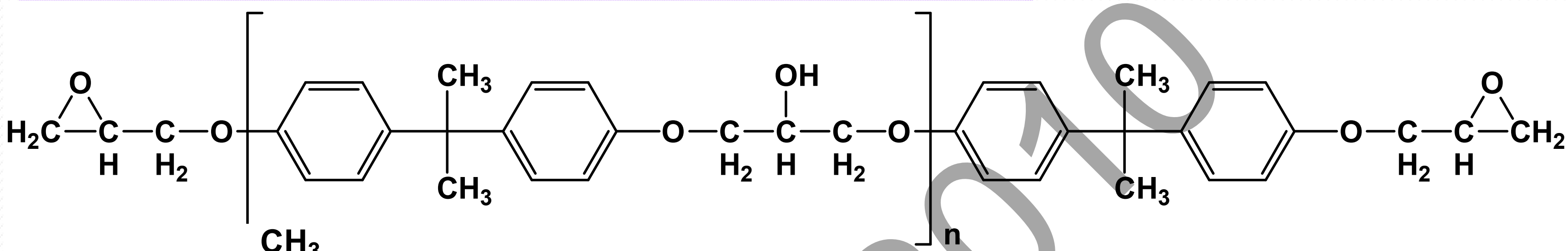
L ~ 1.1 µm, t ~ 1.7 nm, **AR = 200;** 4 layer graphene (G4)

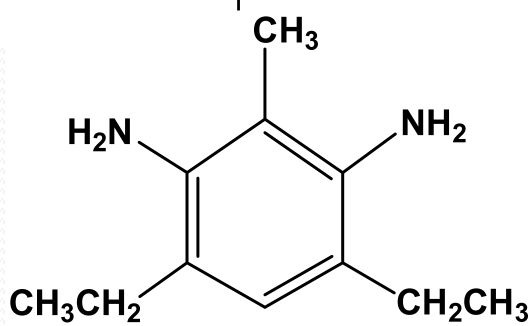
GNP/epoxy composite



Challenges: High loading nano-material dispersion

Epoxy: Diglycidyl ether of bisphenol A





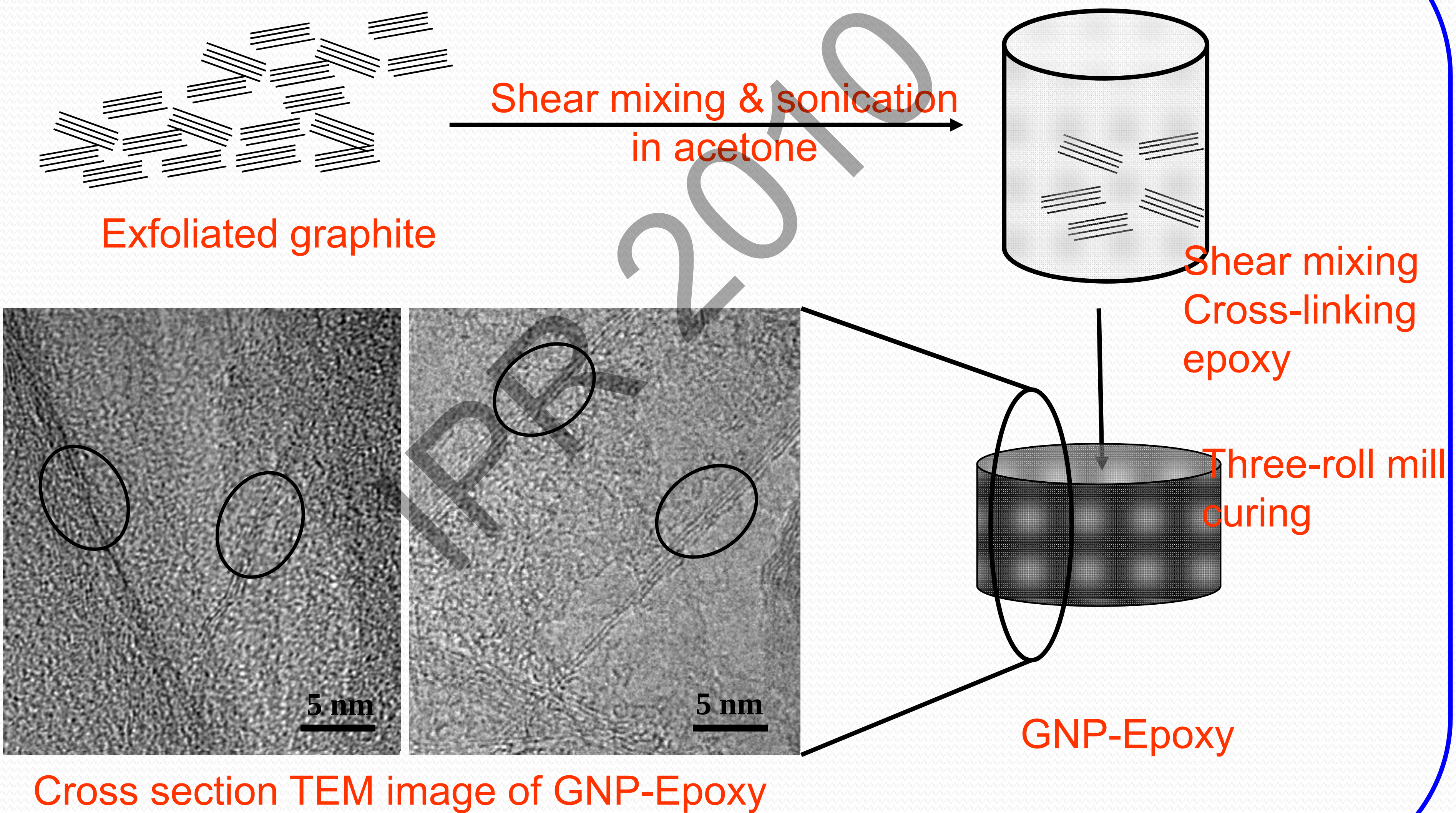
Curing agent:
Diethyl-toluenediamine

Even in lab scale, mechanical stirring is not enough

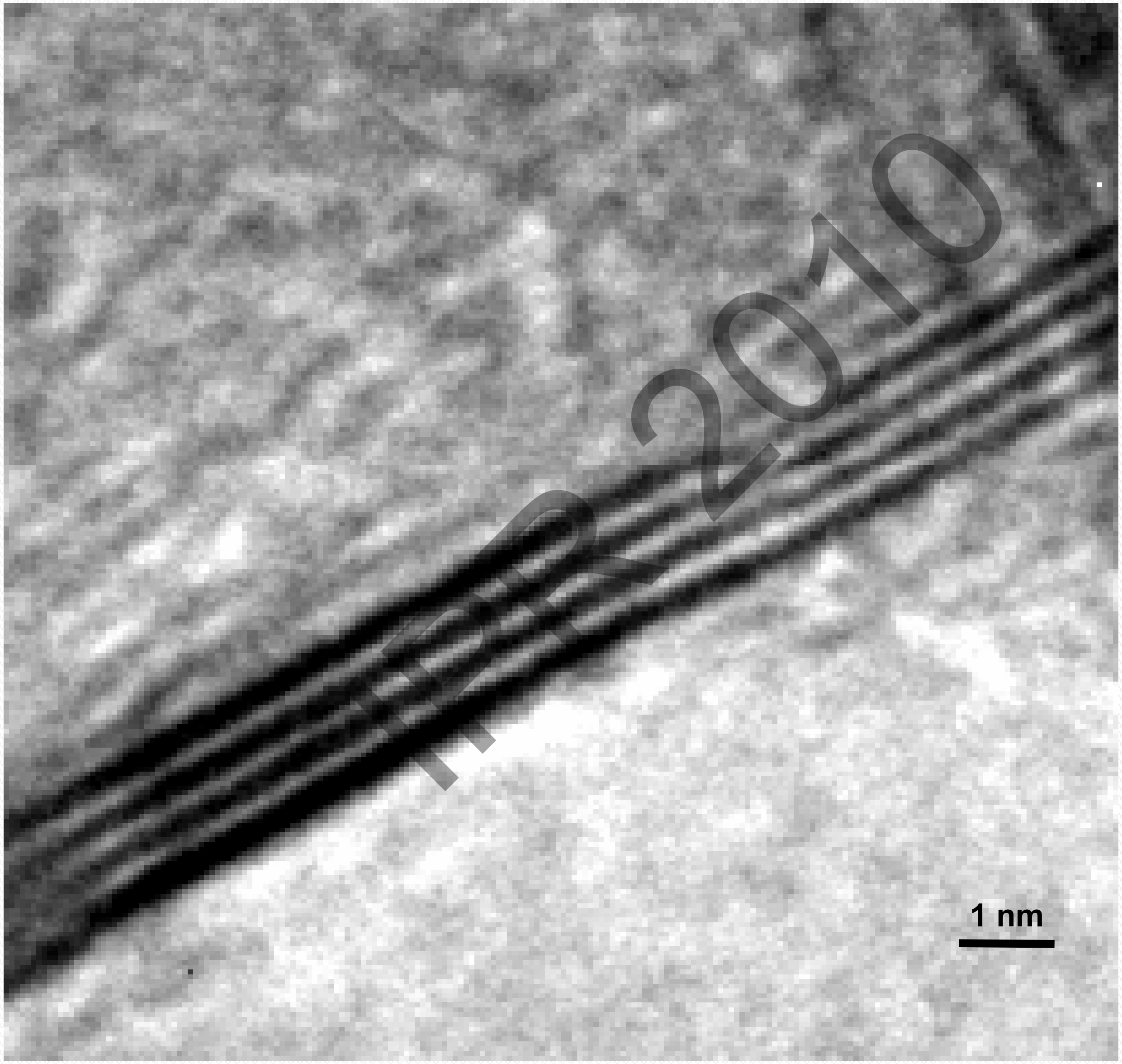
Homogenizer: Shear mixing

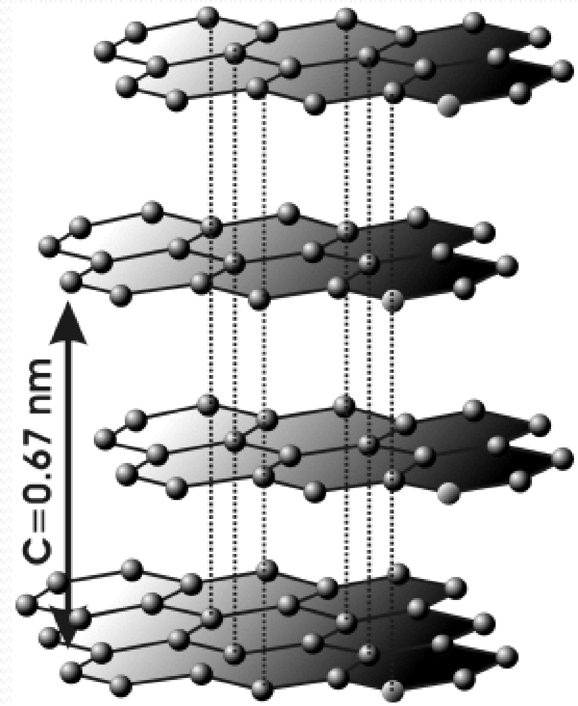
Three roll mill

Schematic show of the composite process



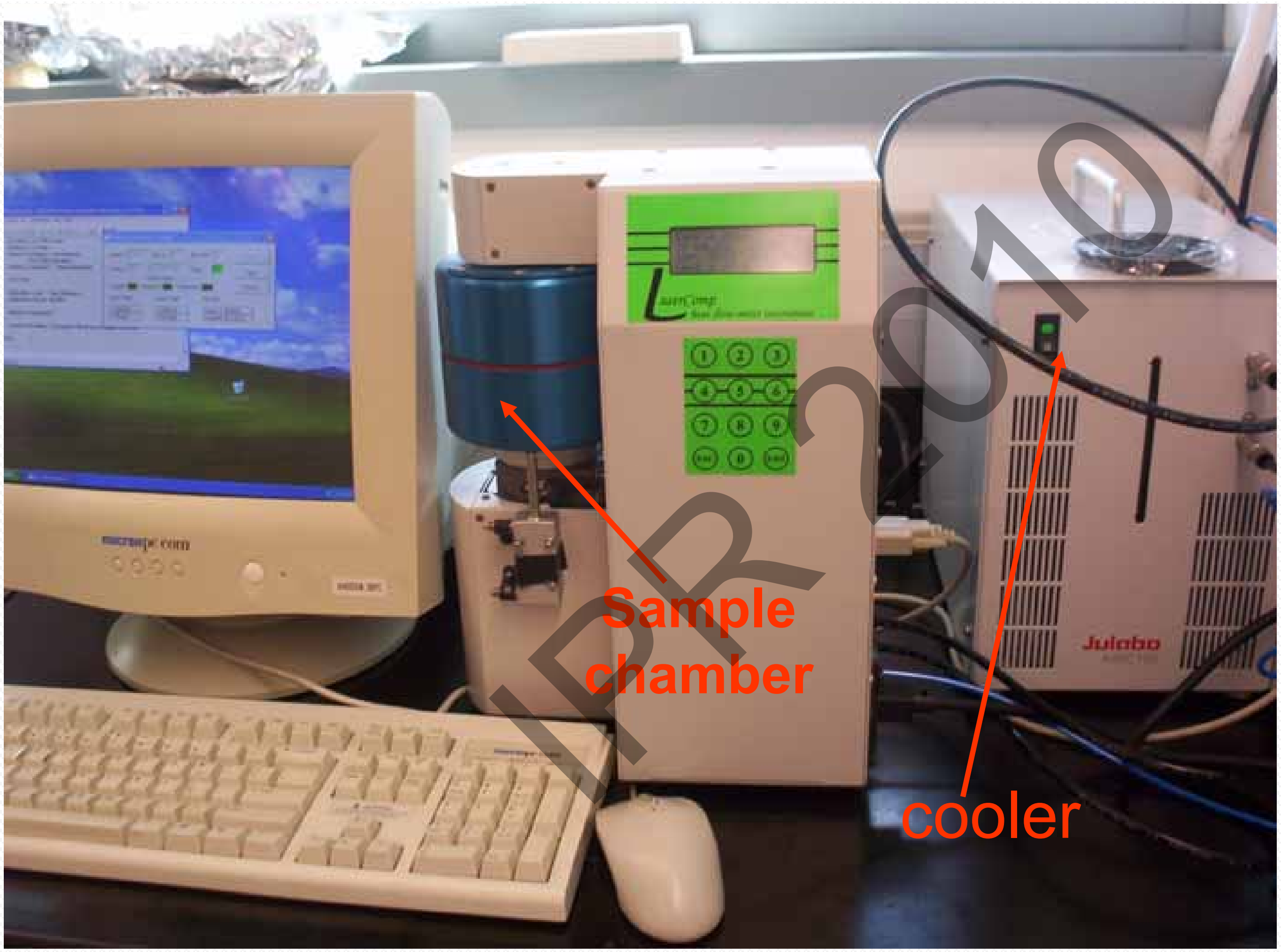
High resolution TEM of GNP in epoxy matrix





L ~ 1.1 μm, t ~ 1.7 nm, **AR = 200;** 4 layer graphene (G4)

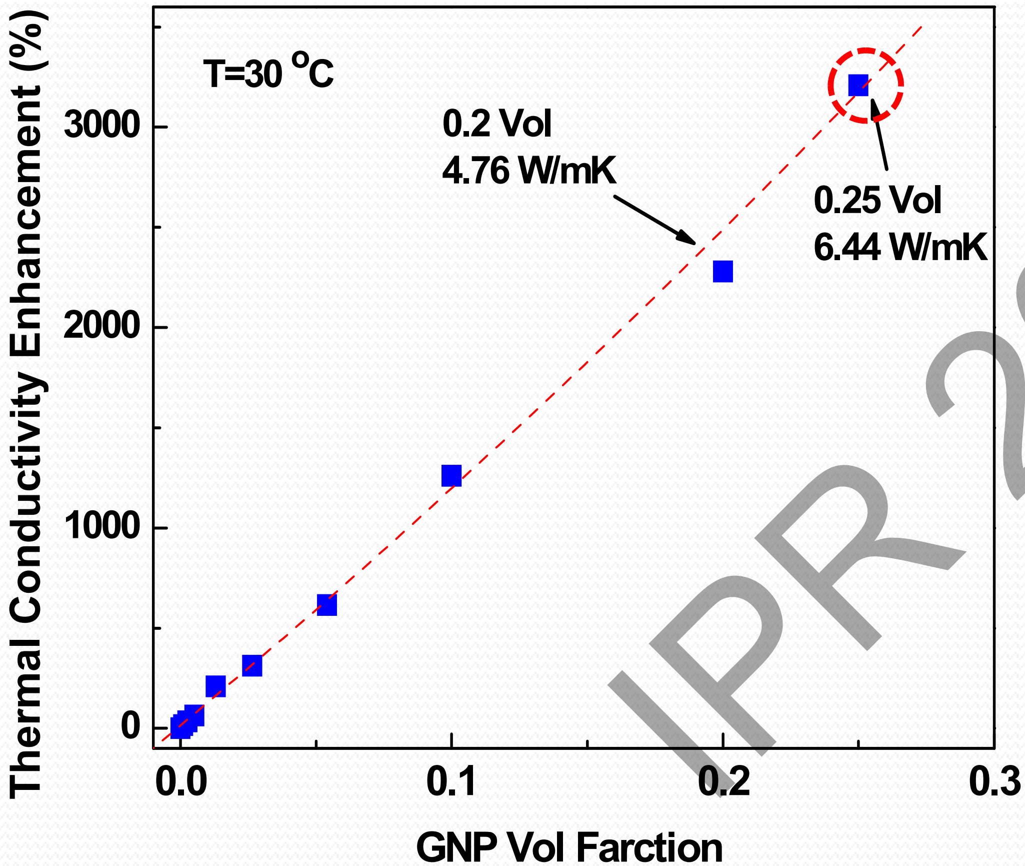
Thermal conductivity measurements: heat flow two thickness testing



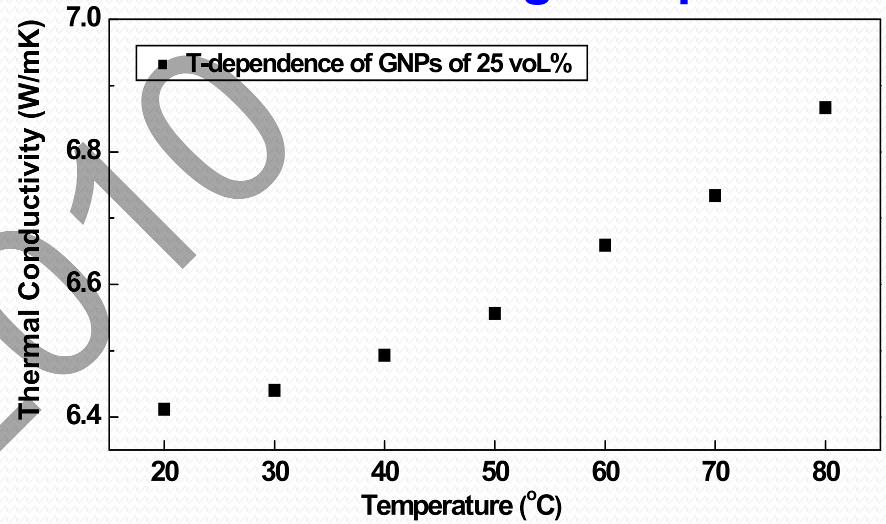
Designed according to ASTM C518-98 From Lasercomp. Inc.

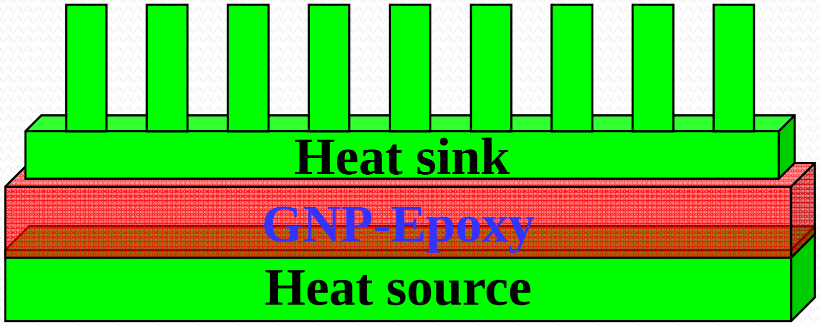
Thermal conductivity of the GNP/epoxy composites

Thermal Conductivity *vs* GNP Ratio



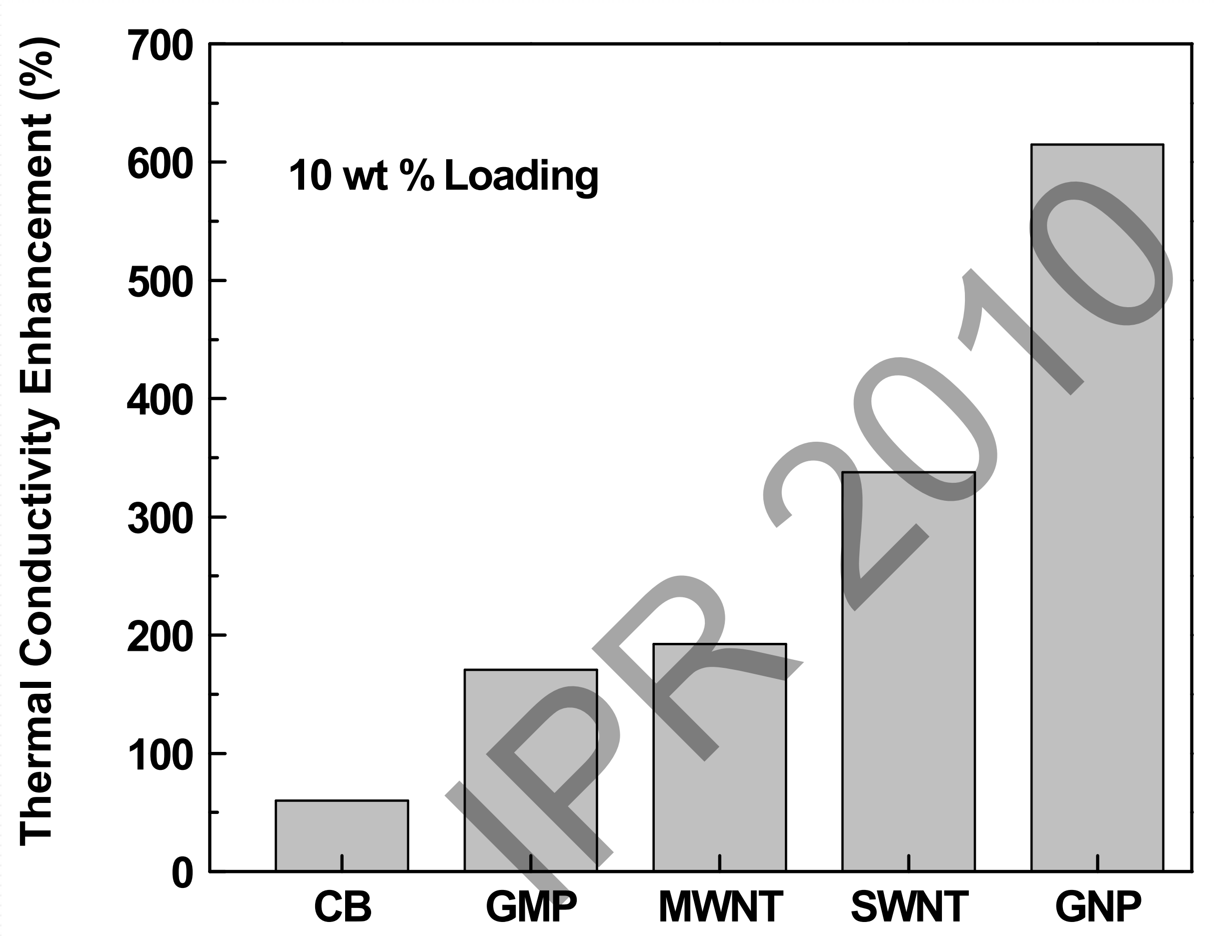
Temperature dependence of 0.25 vol loading composite





- Linear increase of thermal conductivity with filler loading
- Thermal conductivity up to (**10.12 W/mK-40 Vol%**)- suitable for electronic packaging, superior than conventional fillers
- In the T range of computer run, performance is good

Comparison of carbon fillers



CB- carbon black
GMP- graphite microplatelet
MWNT-Multi-Walled Carbon Nanotubes
SWNT- Single-Walled Carbon Nanotubes
GNP- graphite nanoplatelet

- GNPs filler perform better than other carbon fillers
- GNP shows: **130% enhancement / 1 vol.% – efficient filler**
  Whereas it is 20-30% for conventional fillers

Reason: High aspect ratio and rigid 2D structure of – High performance

Modeling prediction & discrepancy

1. Inverse Rule of Mixtures

$$1/K=\Phi_1/k_1+ \Phi_2/k_2$$

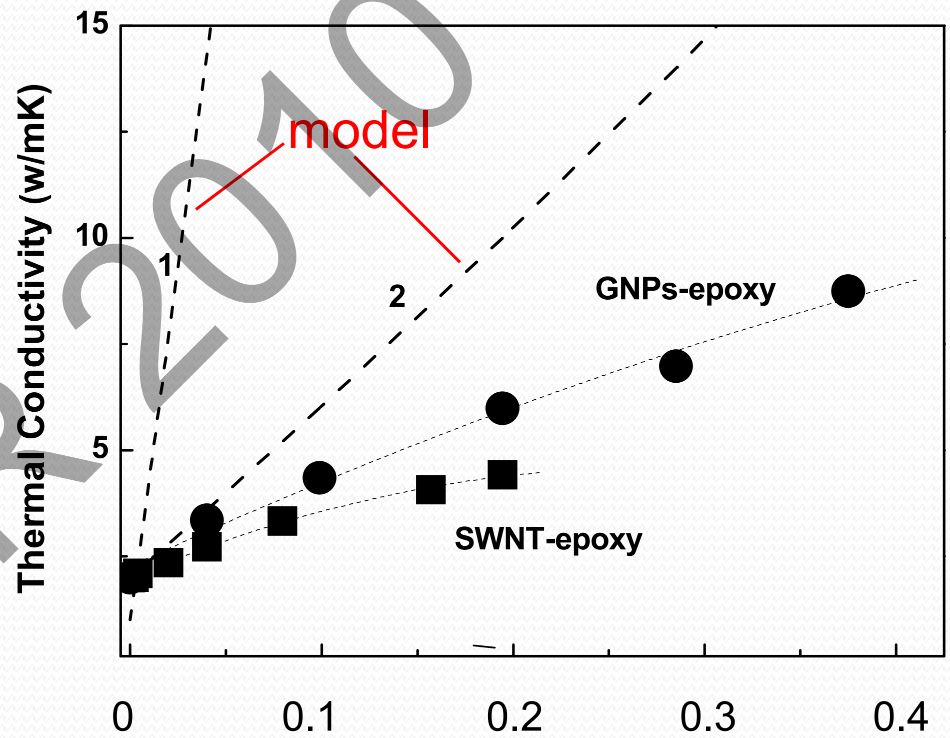
2. Nielsen's model accounts for the geometry of the fillers

$$\frac{K_c}{K_p} = \frac{1+AB\phi_f}{1-B\psi\phi_f}$$

$$A = k_E - 1$$

$$B = \frac{Kf / K_p - 1}{Kf / K_p + A}$$

$$\psi = 1 + \left(\frac{1-\phi_m}{\phi_m^{\ 2}}\right)\phi_f$$

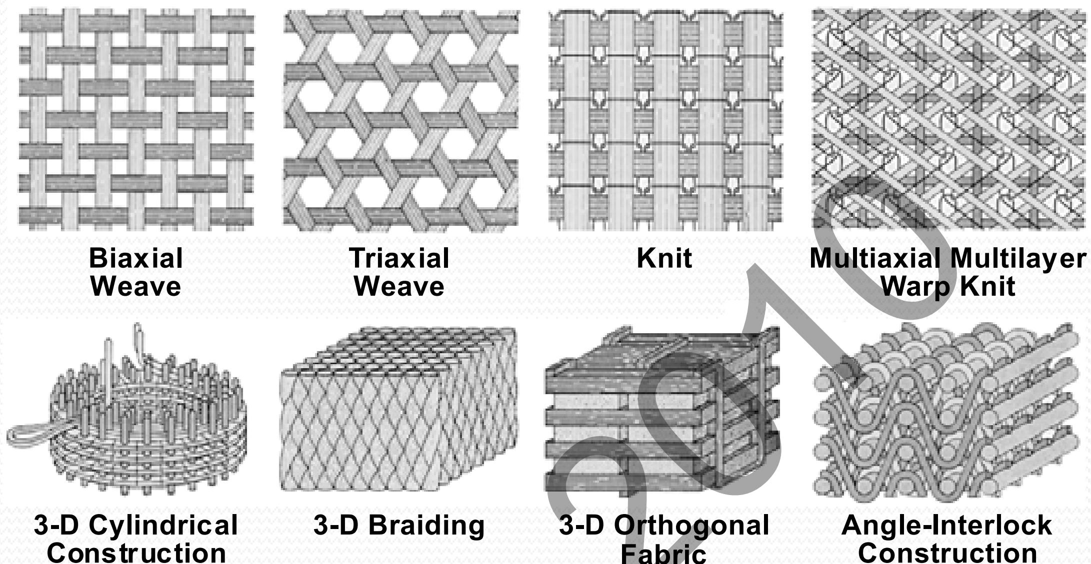


Experimental data are significantly lower than modeling prediction;
The model needs modification for nanomaterials

Summary of 2D-GNP/epoxy composite

- Thermal conductivity of GNP-epoxy resin composite is high up to 10.12 W/mK, which is excellent for thermal interface material application.
- Cost effective production: Graphite $50/Kg
- Highest filler efficiency using rigid 2D fillers

3 D Multi-functional Composites

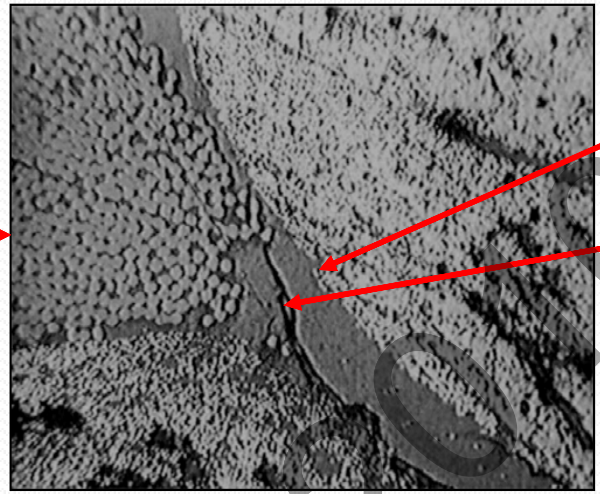


T. W. Chou and F. Ko, *Textile Structural Composites*, Elsevier Sci., Amsterdam, 1988

Boeing 787 Dreamliner: composite materials for half of the parts, next generation Airplane material is not metal, will be carbon fiber matrix

Motivation and Objective

Carbon fiber – Kelvar –
Polymer composite



Matrix rich region

Crack

T. W. Chou, F. Ko,
Textile Structural
Composites, 1988

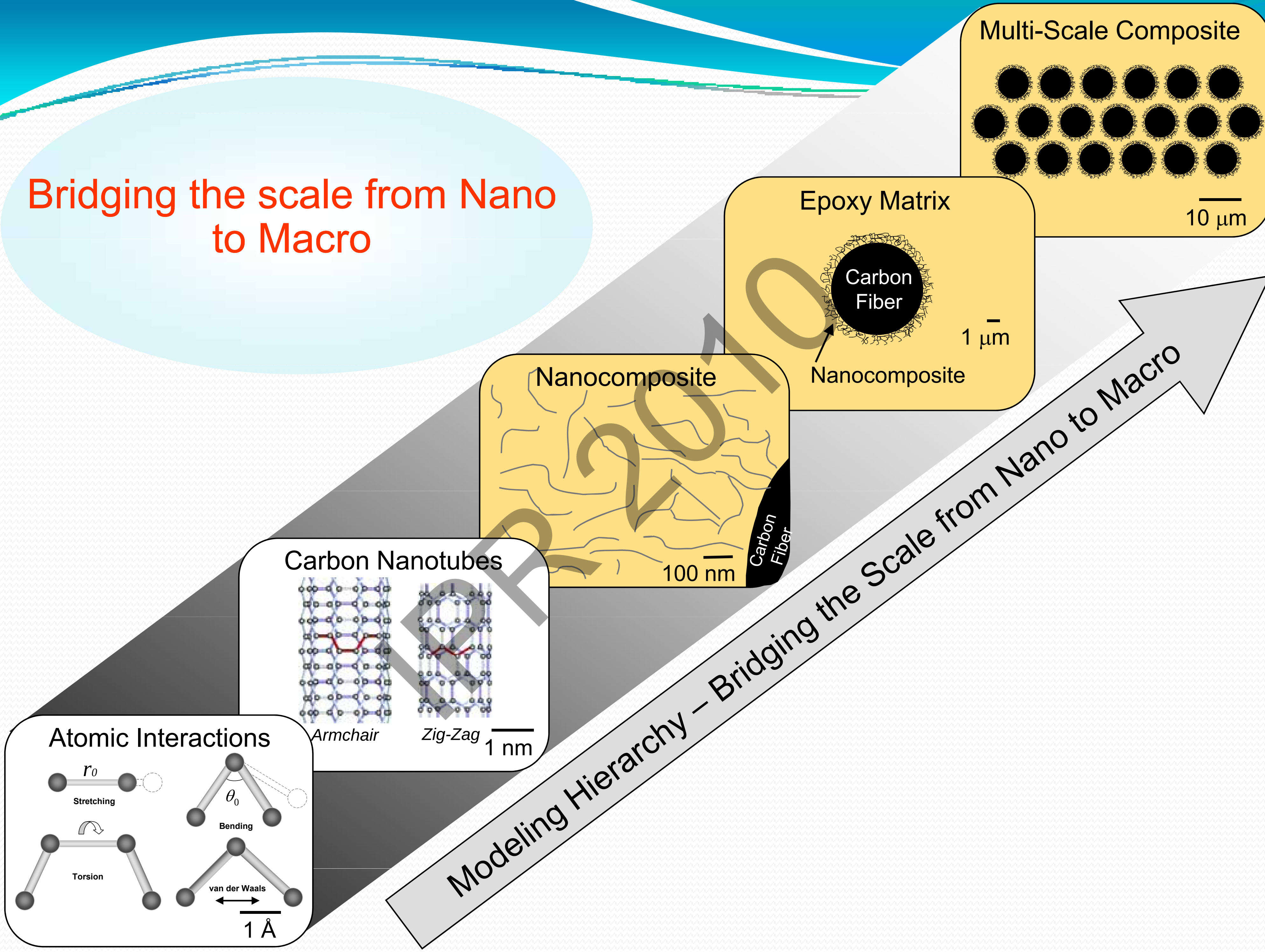
Motivation:

Matrix rich regions form defect in the carbon fiber - polymer composite
Cracking and failure usually start and propagate from these defect sites

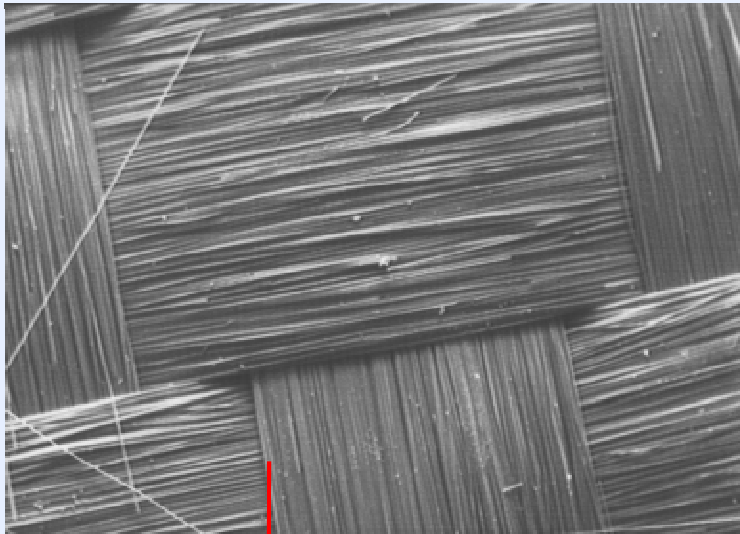
Approach:

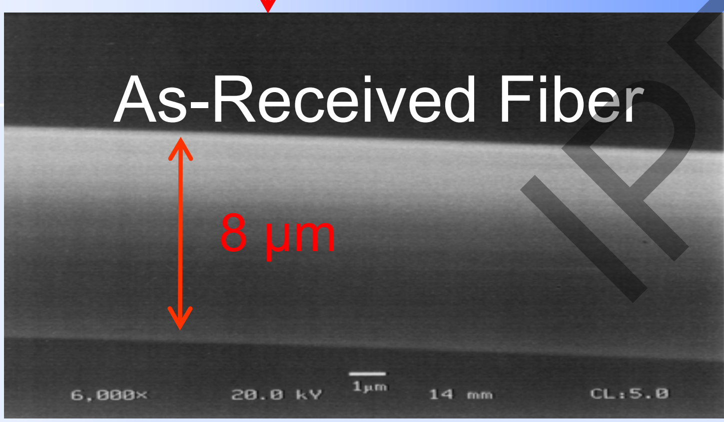
Carbon nanotube to reinforce matrix regions and void the defect in composite
Increase the carbon fiber – polymer interfacial interaction and load transfer

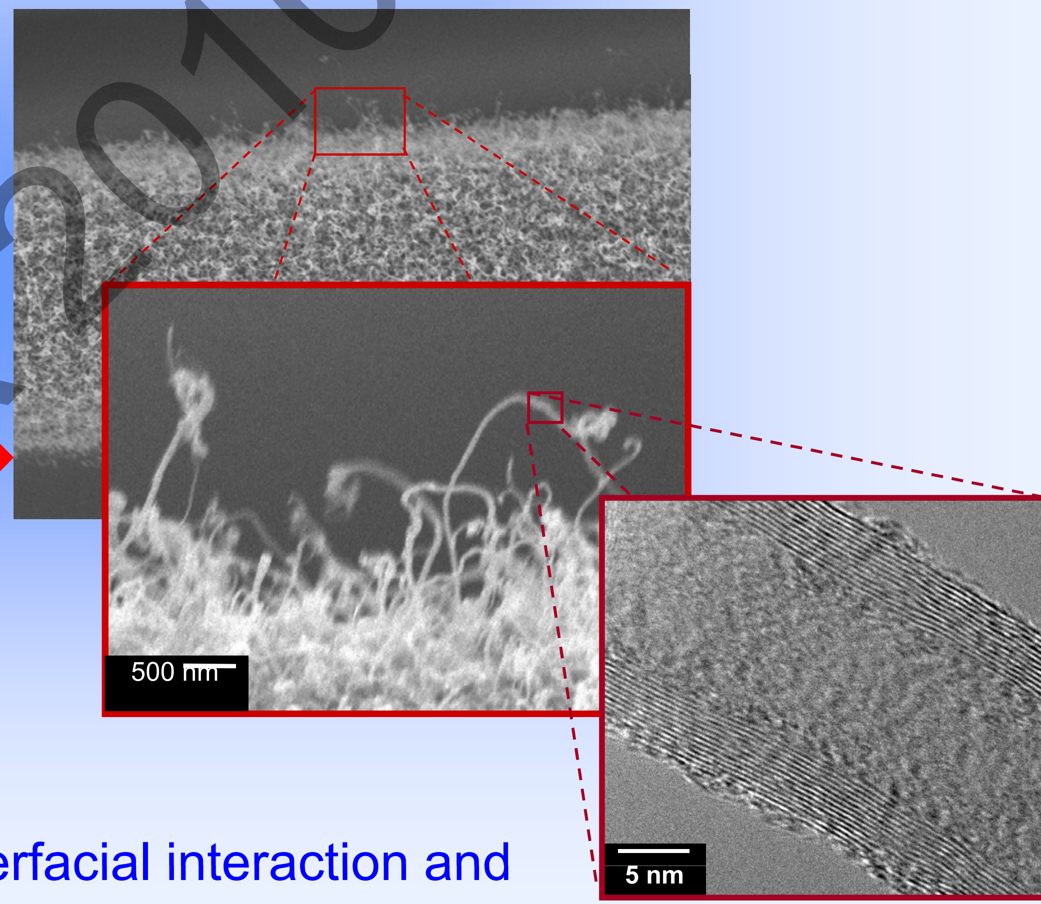
Bridging the scale from Nano to Macro



Strategy



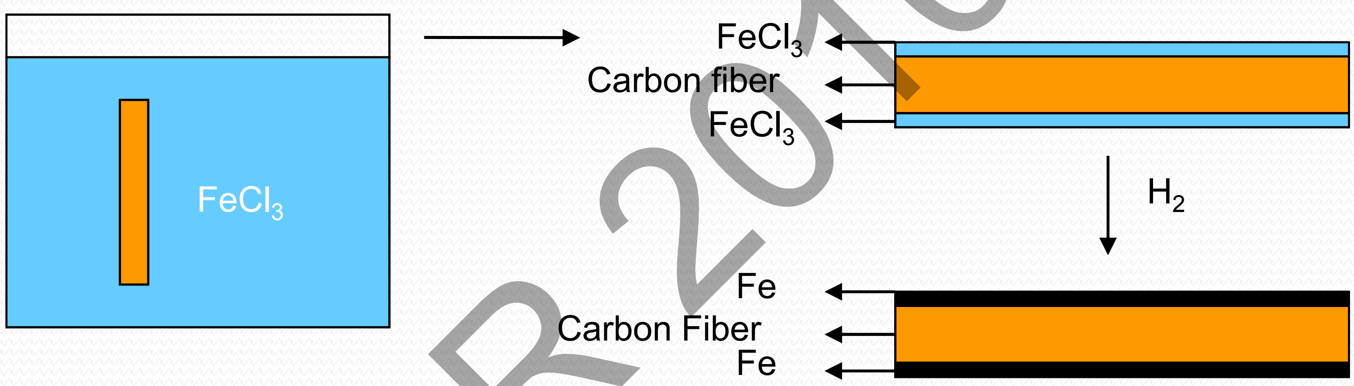


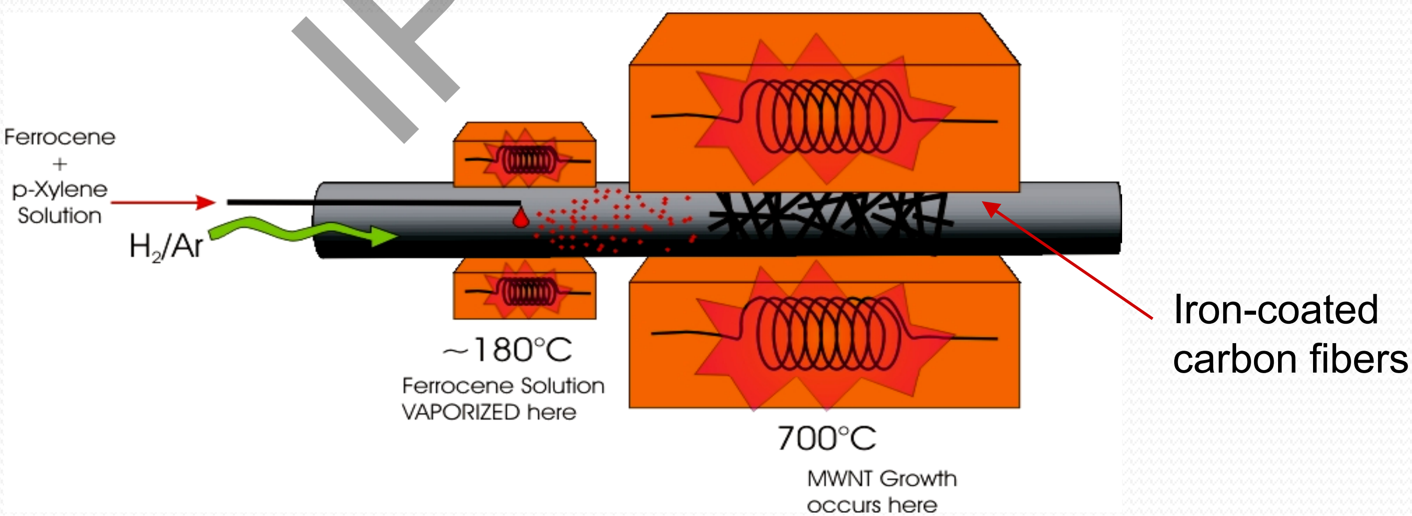


CNT reinforcement increases the interfacial interaction and the loading transfer and can avoid fiber pull-out

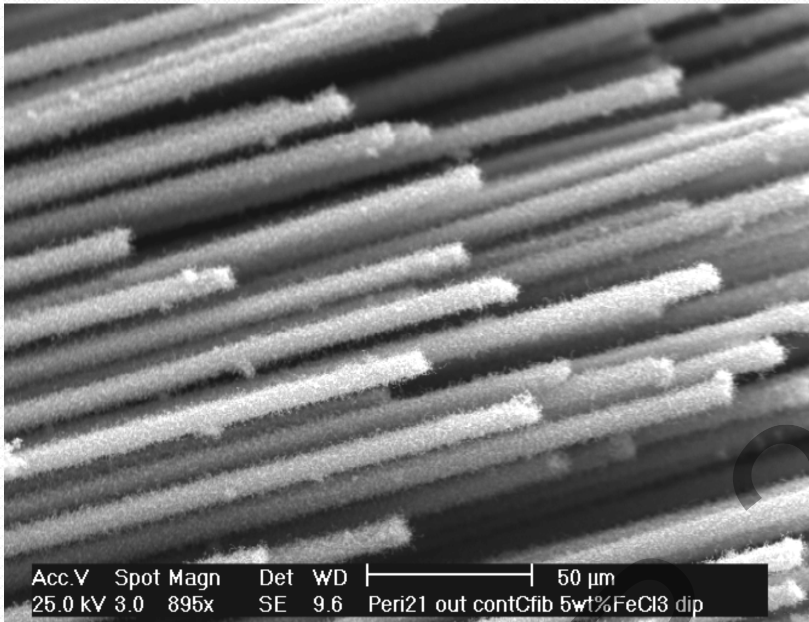
CVD Deposition of CNTs on Carbon Fiber/Fabrics

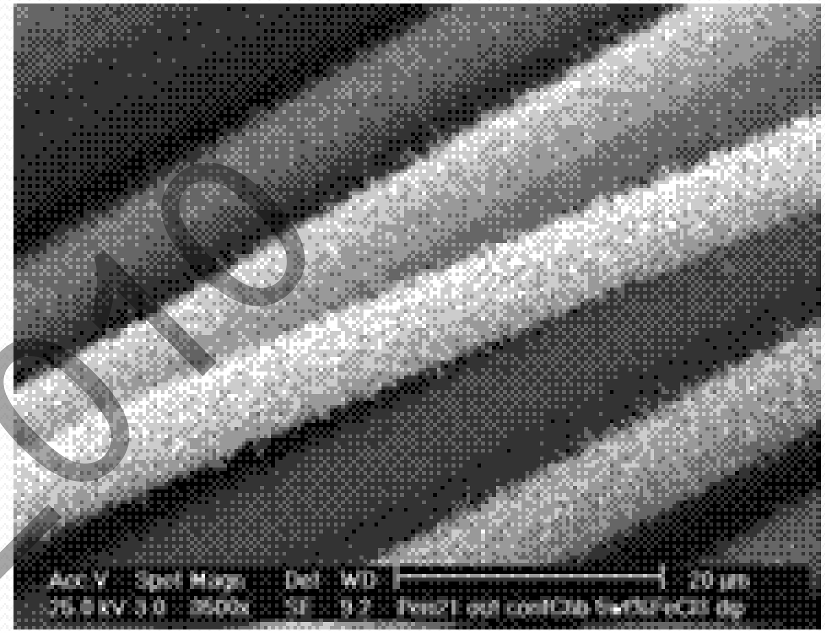
-deposition of iron (Fe) for selective growth of CNTs

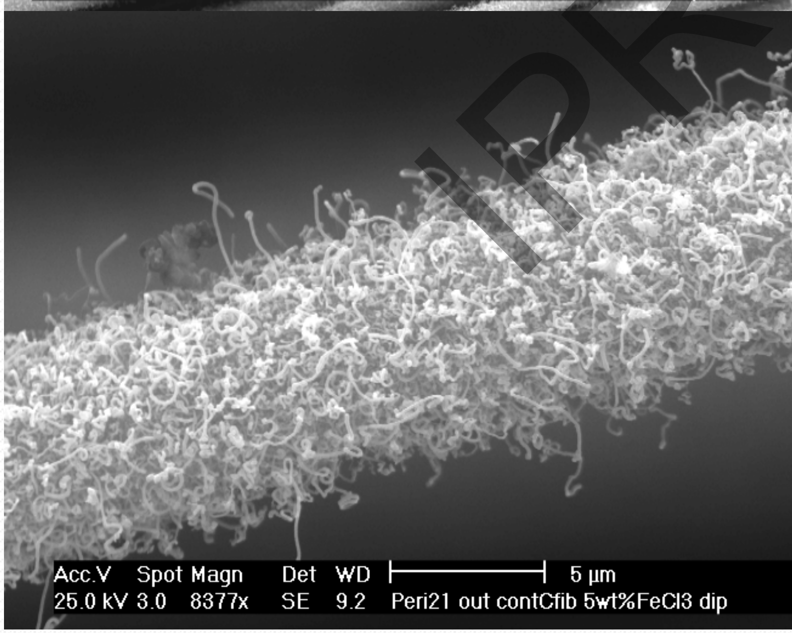


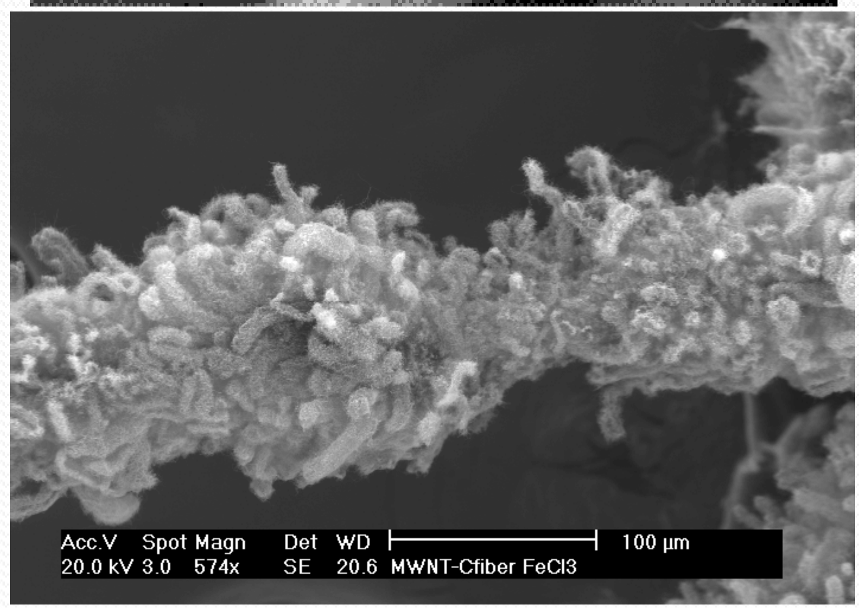


SEM of Carbon Fibers Coated with CVD-grown CNTs





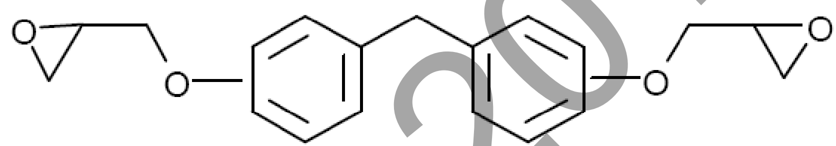




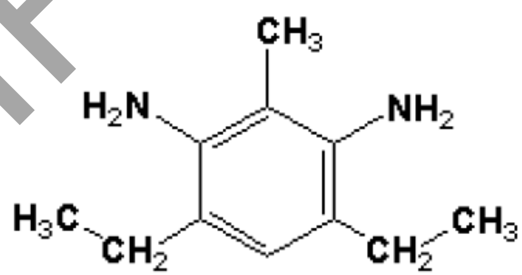
Epoxy resin system

EPON 862 – EPI-Cure W Curing Agent
(Resolution Performance Products, Inc.)

Bisphenol-F Epichlorohydrin Epoxy

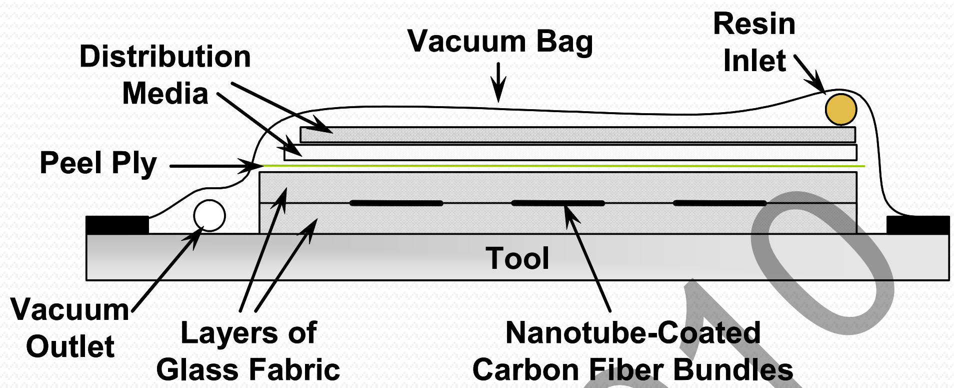


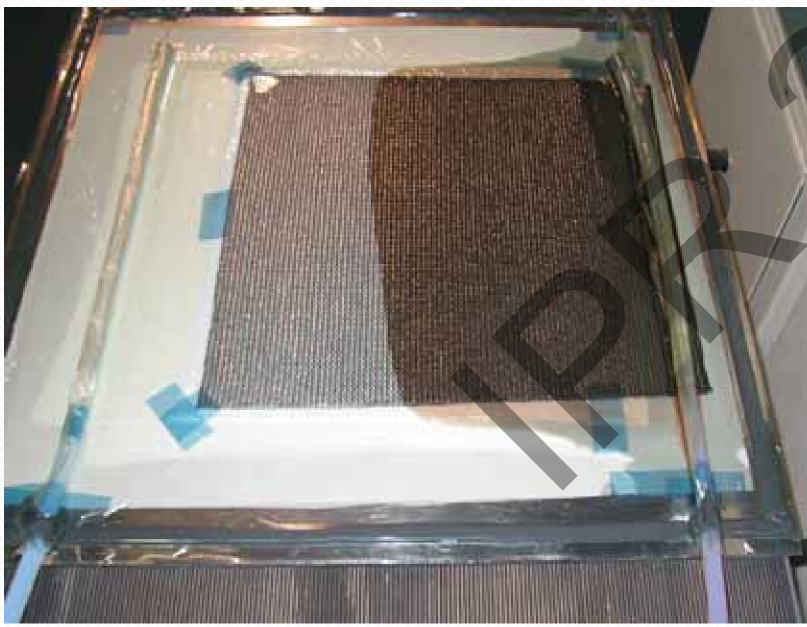
Aromatic Diamine (diethyltoluenediamine)

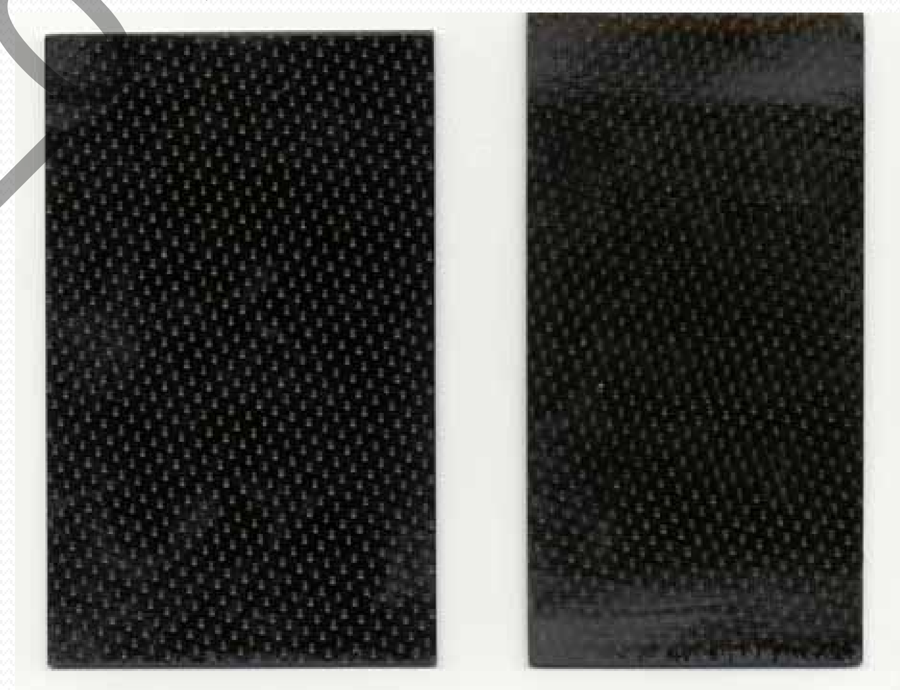


Amine hydrogen equivalent wt (AHEW) 43-46

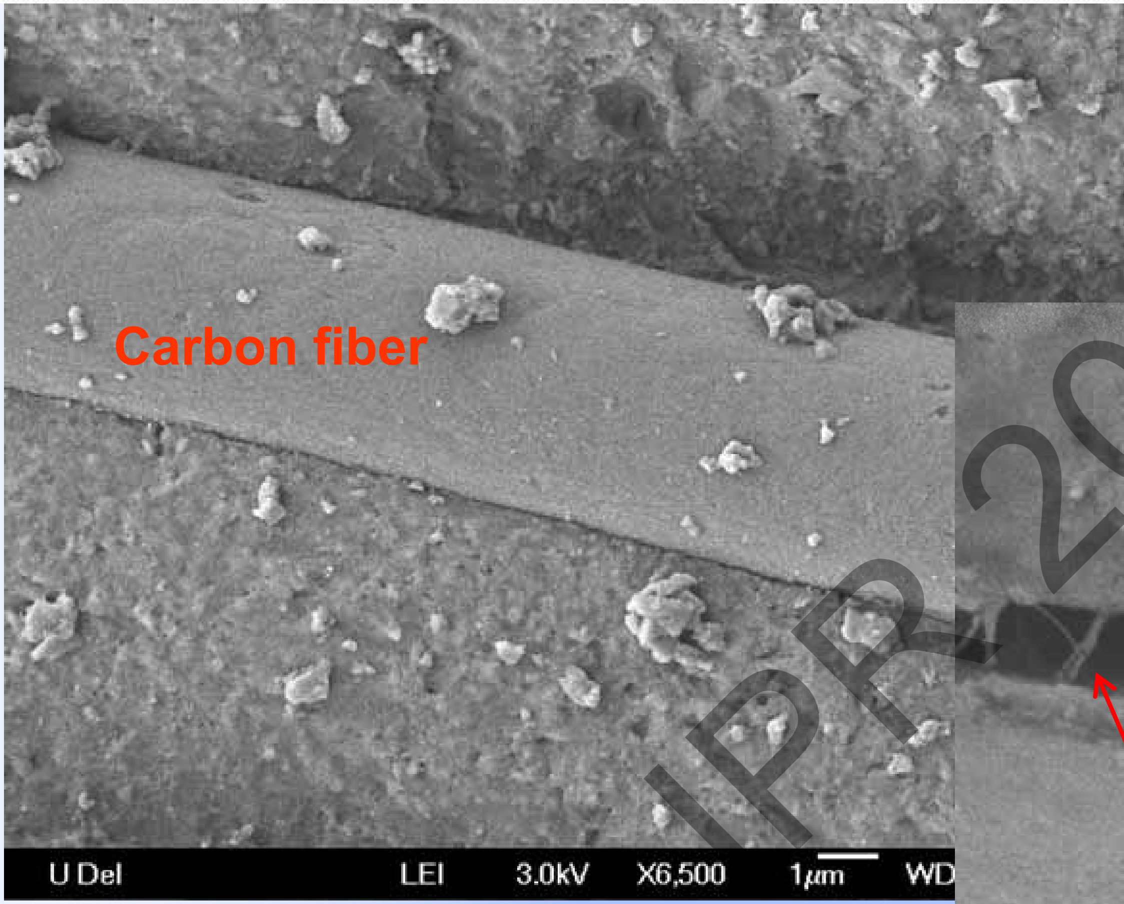
Vacuum assisted infusion

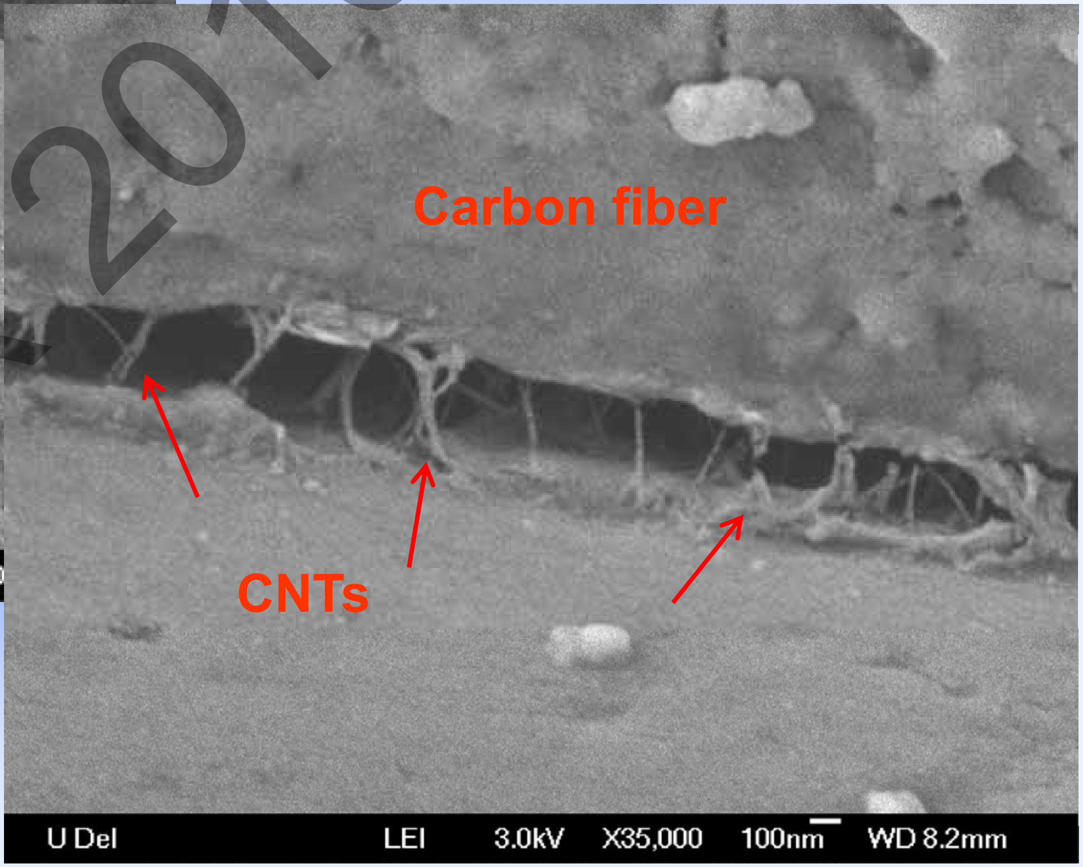




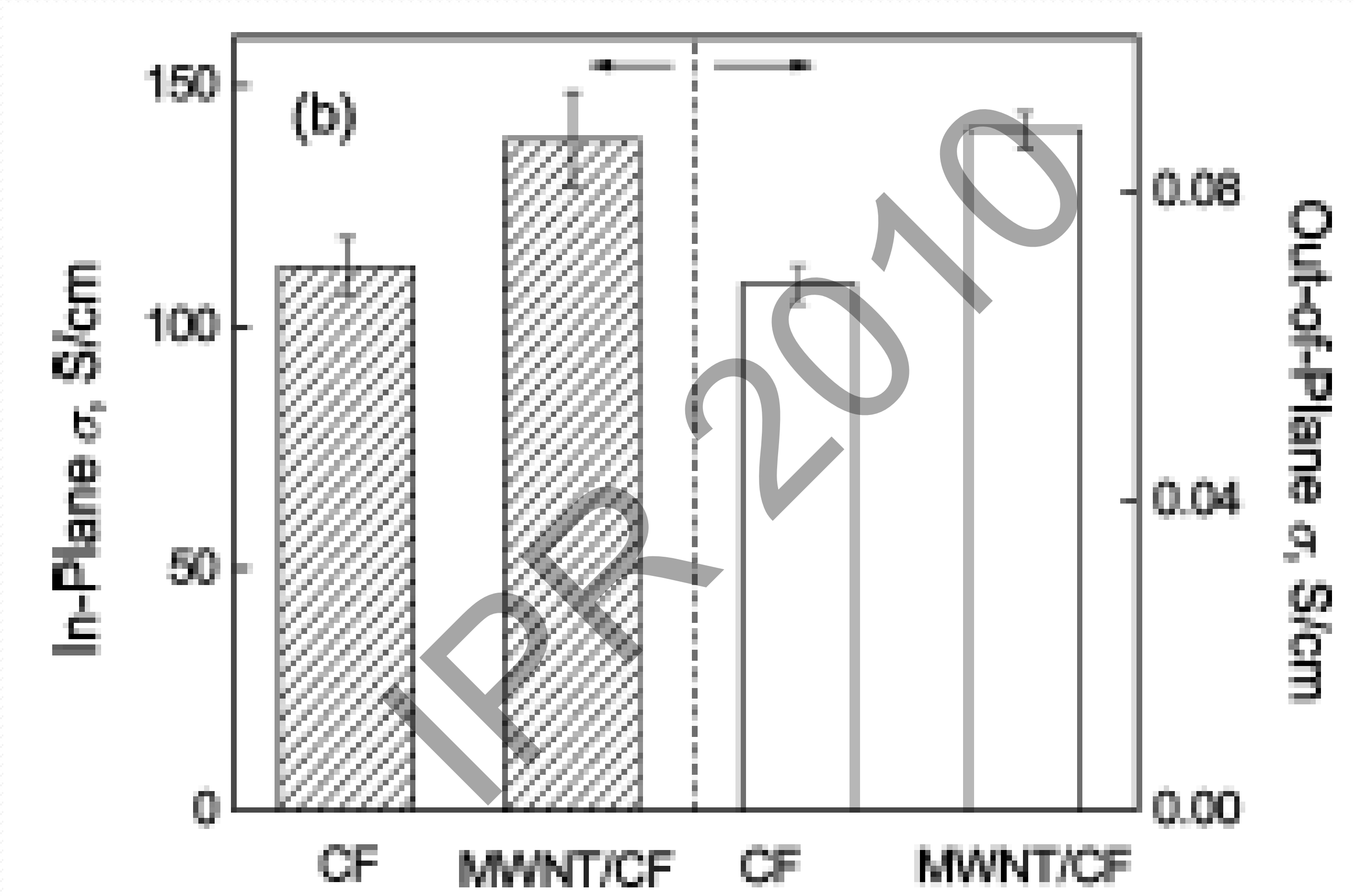


SEM observation of the composite



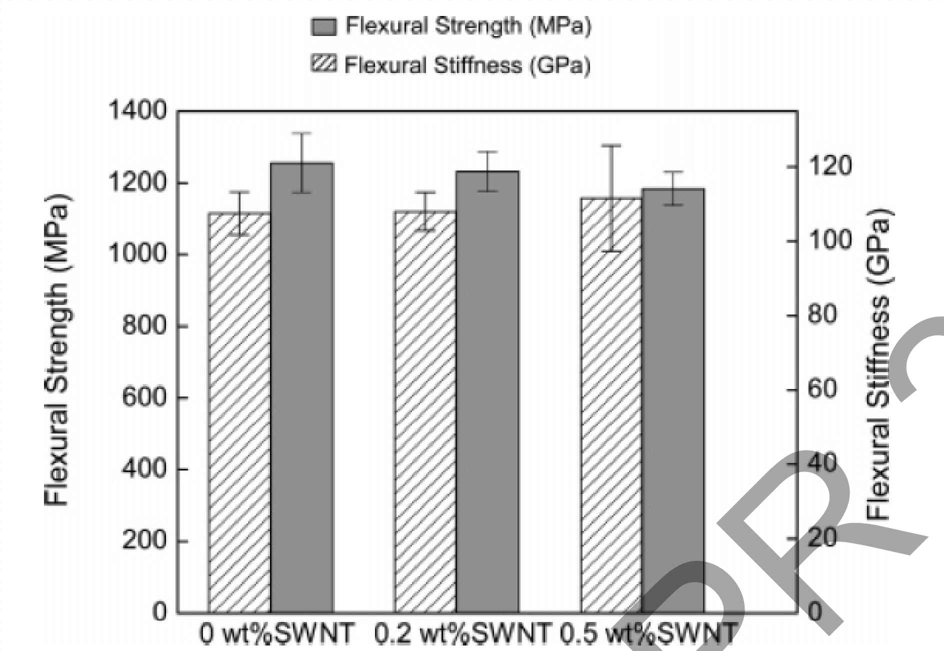


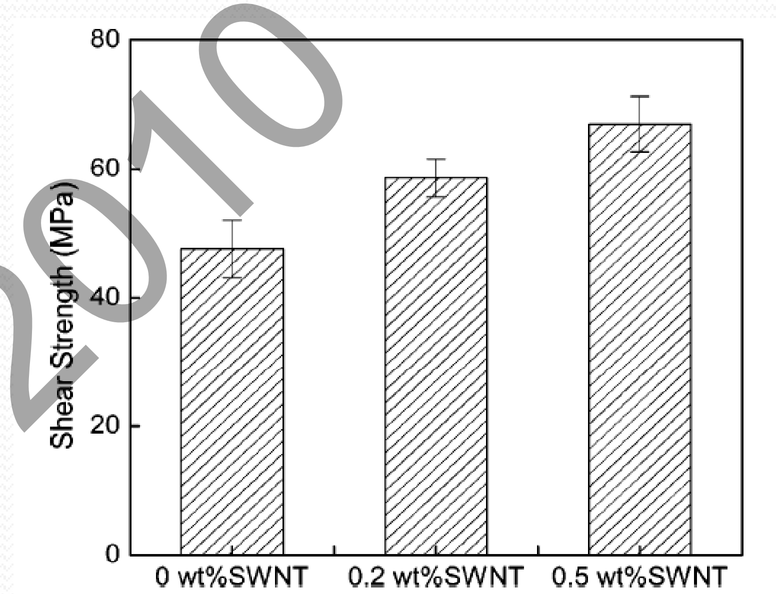
Electrical conductivity enhancement



Both in-plane and out-plane electrical conductivity increased about 17 % @ 0.5 wt% CNTs loading

Mechanical properties enhancement





Flexural strength and stiffness of CF/epoxy composites with and without CNTs were slightly improved.

Shear strength of CF/epoxy composites with and without CNT was enhanced at 35% (loadings of 0.2 and 0.5 wt %).

Summary

- CNTs had been deposited on carbon fiber surface

- Both in-plane and out-plane electrical conductivity increased about 17 %

- Flexural strength and stiffness were slightly improved and shear strength of the carbon fiber epoxy was enhanced at 35% with 0.5 wt % of CNTs.

SABIC Innovative Plastics™

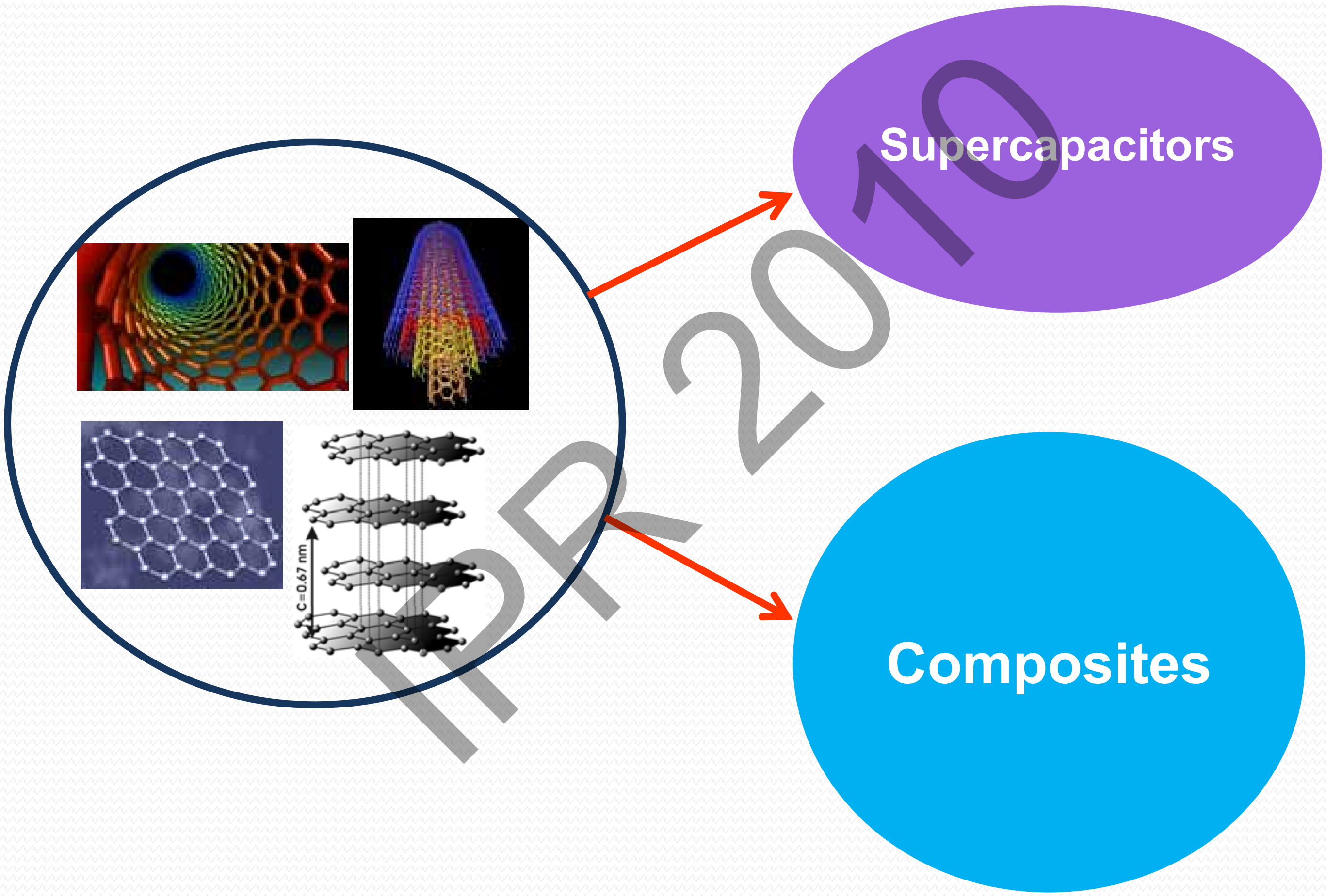
sabic

My work in SABIC Innovative Plastics

Aiping Yu

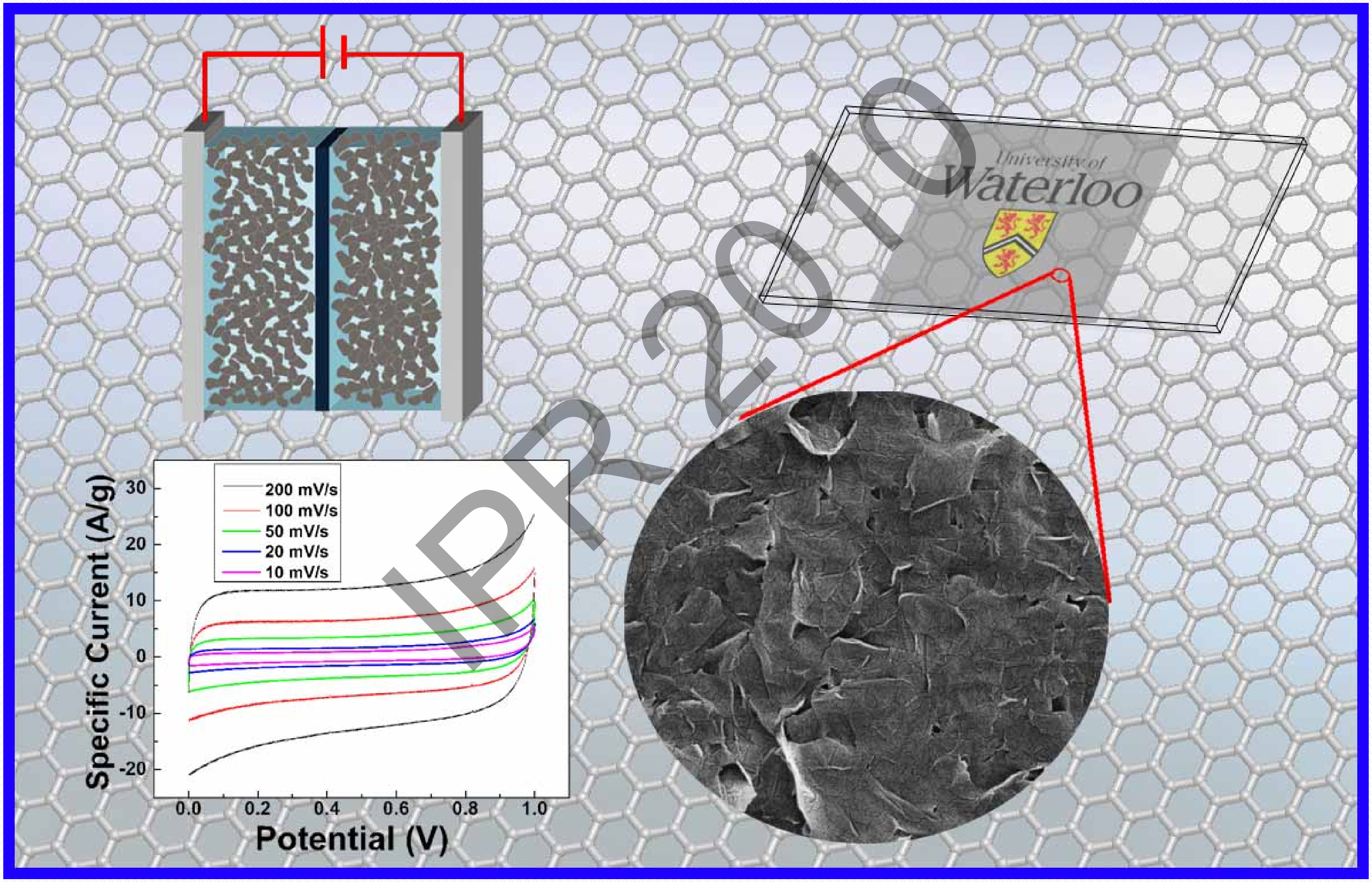
Sharing our future

My work @ uwaterloo



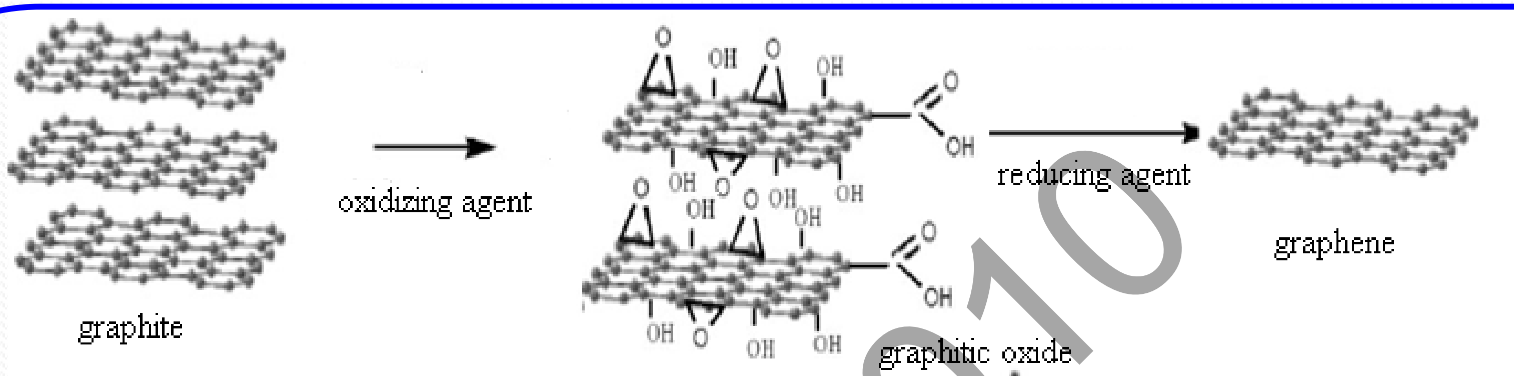
My work @ uwaterloo

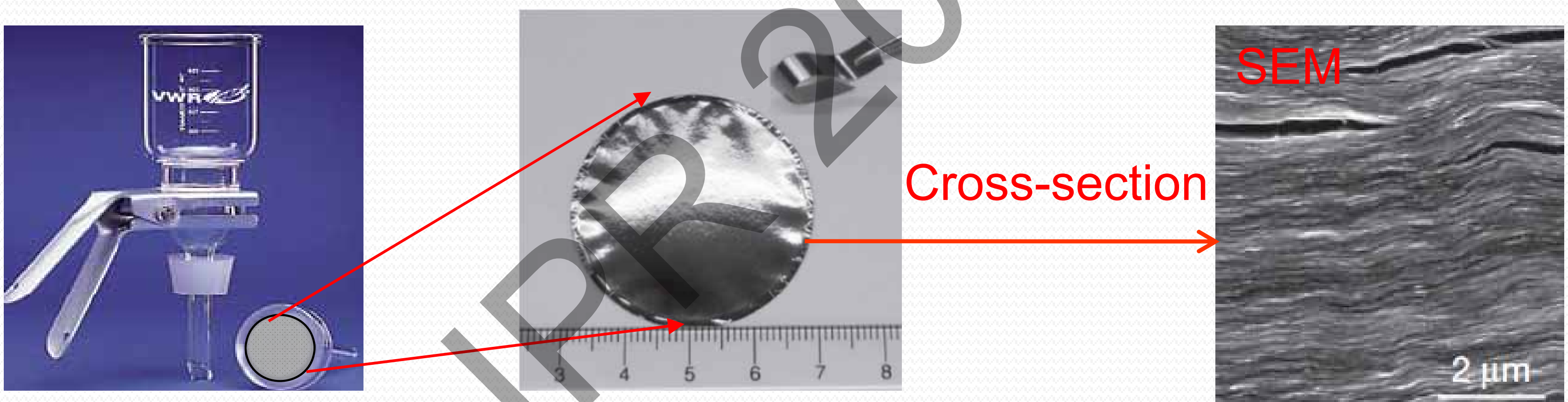
Supecapacitor: a new energy storage device

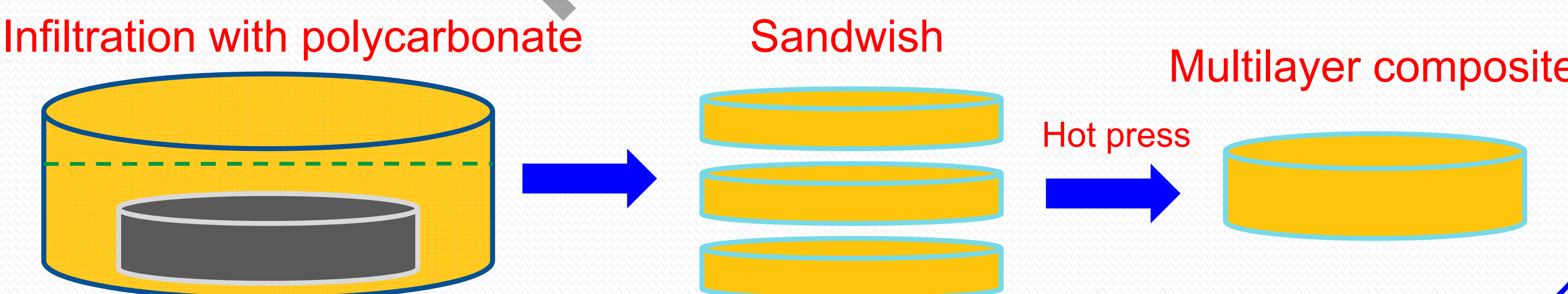


My work @ uwaterloo

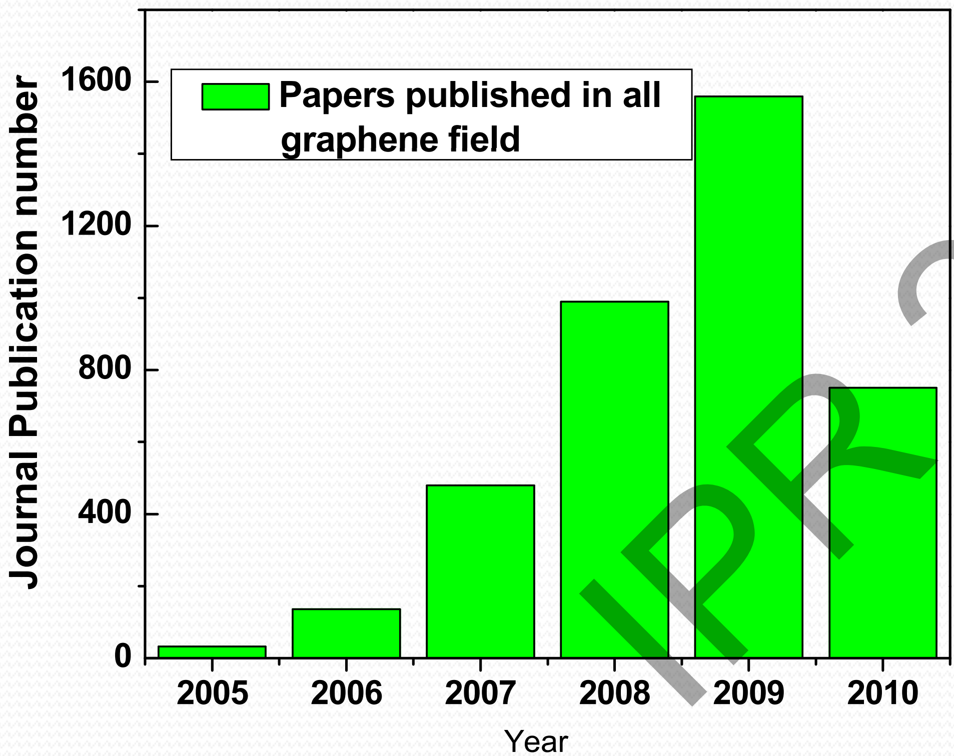
High loading multi-functional graphene/polycarbonate composite

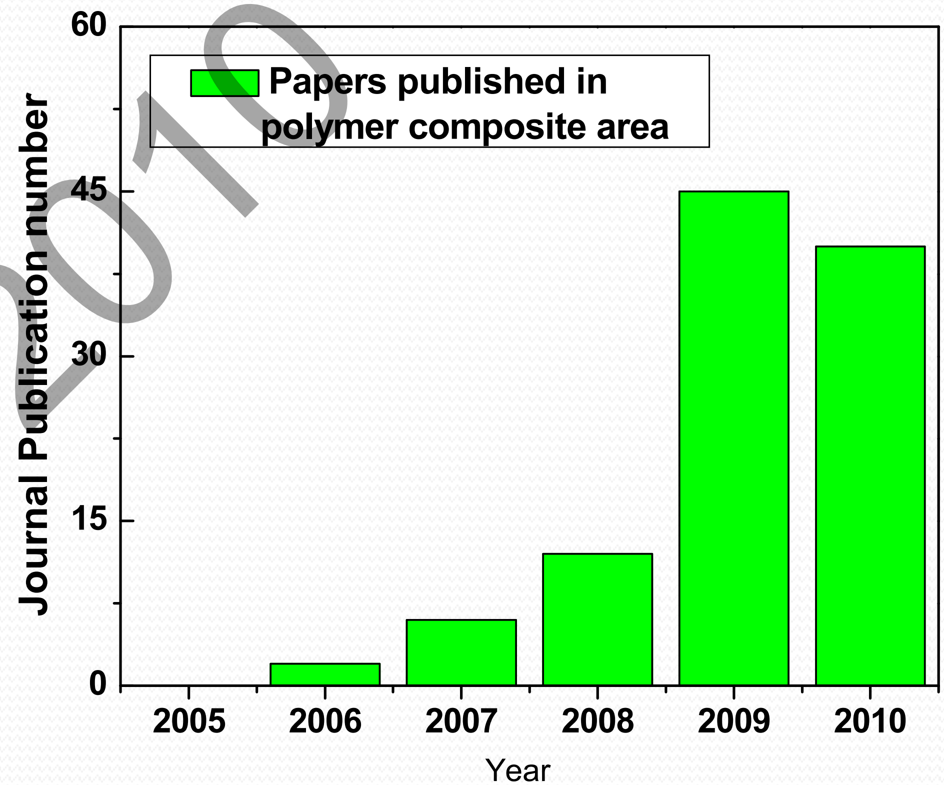




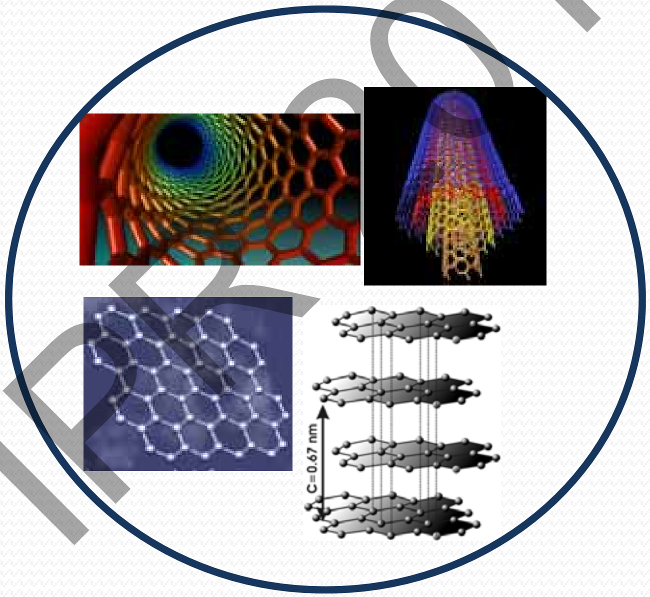


Recent publications of graphene





Welcome collaborations and suggestions for applying carbon nanotubes and graphene to polymer composites



Thanks a lot for your attention