Graphene Nanoplatelets: A Multi-functional Nanomaterial Additive for Polymers and Composites

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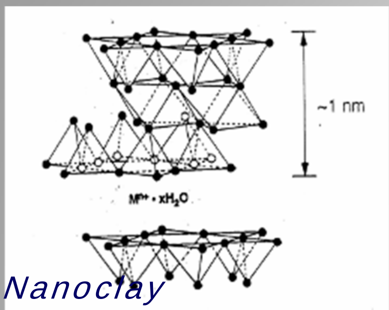
THE MATERIAL DIFFERENCE

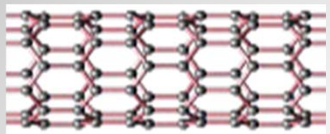
Outline

- xGnP Properties and Synthesis
- Dispersion and Processing in Polymers
- Multifunctional Nanocomposite Properties
- Nano-Structuring xGnP
  - 1D, 2D and 3D Morphologies
- xGnP 'Paper' and Films
- Energy Applications
  - Batteries, Supercaps, Solar Cells, Fuel Cells
- XG Sciences-Path to Commercialization

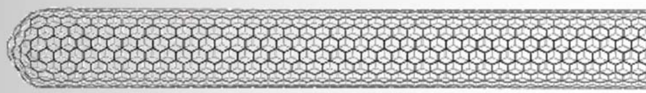
Nano-Materials Portfolio

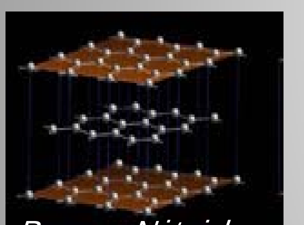


Nanoclay


Carbon Nanotubes

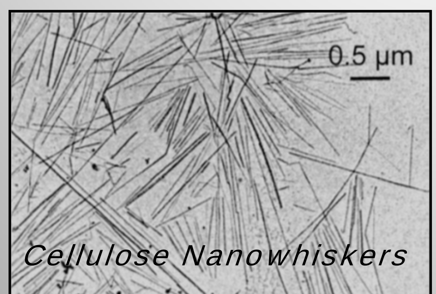
Vapor Grown Carbon Fibers


Boron Nitride Nanotubes


Boron Nitride NanoPlatelets

xGnP Graphene NanoPlatelets

Halloysite Nanotubes



Cellulose Nanowhiskers

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	Carbon Nanotube	Graphene NanoPlatelets
PHYSICAL STRUCTURE	Cylinder ~1nm X 100nm	Platelet ~1nm X 100nm
CHEMICAL STRUCTURE	Graphene (chair, zigzag, chiral)	Graphene
INTERACTIONS	π - π	π - π
TENSILE MODULUS	1.0-1.7 TPa	~1.0 TPa
TENSILE STRENGTH	180 Gpa	~(10-20 GPa)
ELECTRICAL RESISTIVITY	~ 50×10^{-6} Ω cm	~ 50×10^{-6} Ω cm ∥ ~ 1 Ω cm ⊥
THERMAL CONDUCTIVITY	3000 W/m K	3000 W/m K ∥ 6 W/m K ⊥
COEF THERMAL EXP.	-1×10^{-6}	-1×10^{-6} ∥ 29×10^{-6} ⊥
DENSITY	1.2 – 1.4 g/cm^3	~2.0 g/cm^3

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Why the Interest in Graphene and xGnP?

- **Nano-Material**
  - **High Surface Area, High Aspect Ratio,**
  - **Nano Thickness, Micro Diameter, Platelet Morphology,**
  - **Low Concentration Required**
  - **Low Cost**
- **Multifunctional Material**
  - **Low Density**
  - **High Stiffness**
  - **Electrical Conductive**
  - **Thermally Conductive**
  - **Low Thermal Expansion**
  - **High Thermal Stability**
  - **Barrier Properties**
  - **Transparent**

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Synthesis of Graphene and xGnP

- **Mechanical Exfoliation of Graphite**

  Novoselov et al., Science 306, 666 (2004)

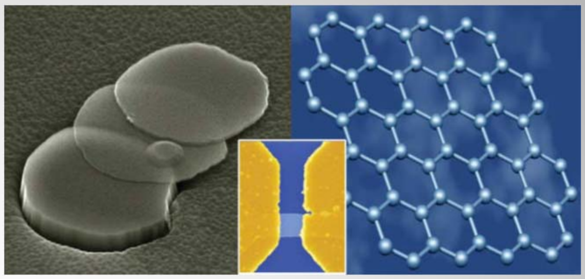
- **Monolayer Synthesis**

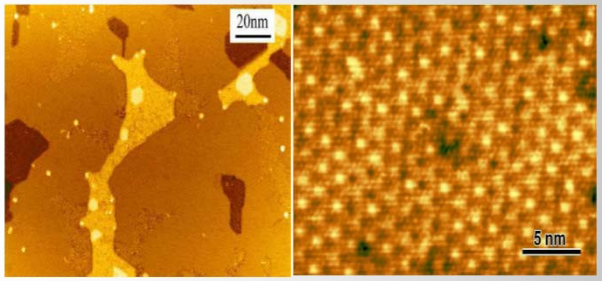
  Walt A. de Heer, et al., Solid State Communications 143 (1-2), 92-100 (2007)

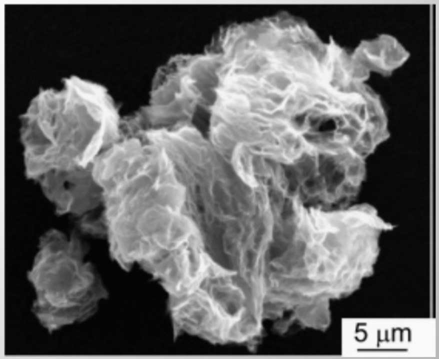
- **Few Layer Exfoliation via graphite oxide and reduction to graphene**

  M. Hirata et al., Carbon 42(14), 2929-2937, 2004

- **Few Layer Intercalation and Exfoliation**







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Graphite Intercalated Compounds

- **Graphite can be a host material for intercalant chemicals**
  Brodie BC. Ann Chim Phys;45:351–3, 1855
  Schafhaeutl C. J PraktChem; 21:129–57, 1840
- **Typical intercalates include:**
  - **alkali metals (Li, Na, K, Rb, Cs),**
  - **metal halides ($FeCl_3$, CrO_3, $TiCL_3$, $PtCl_4$, etc.),**
  - **acids (nitric acid, sulfuric acids, phosphoric acid, perchloric acid, chromic acid, etc)**
  - **combinations of alkali metal/organic molecule (K/THF, Cs/benzene, Cs/ethylene, Cs/styrene, Cs/butadiene, etc.)**
- **Some of the GICs can be exfoliated by rapid heating**

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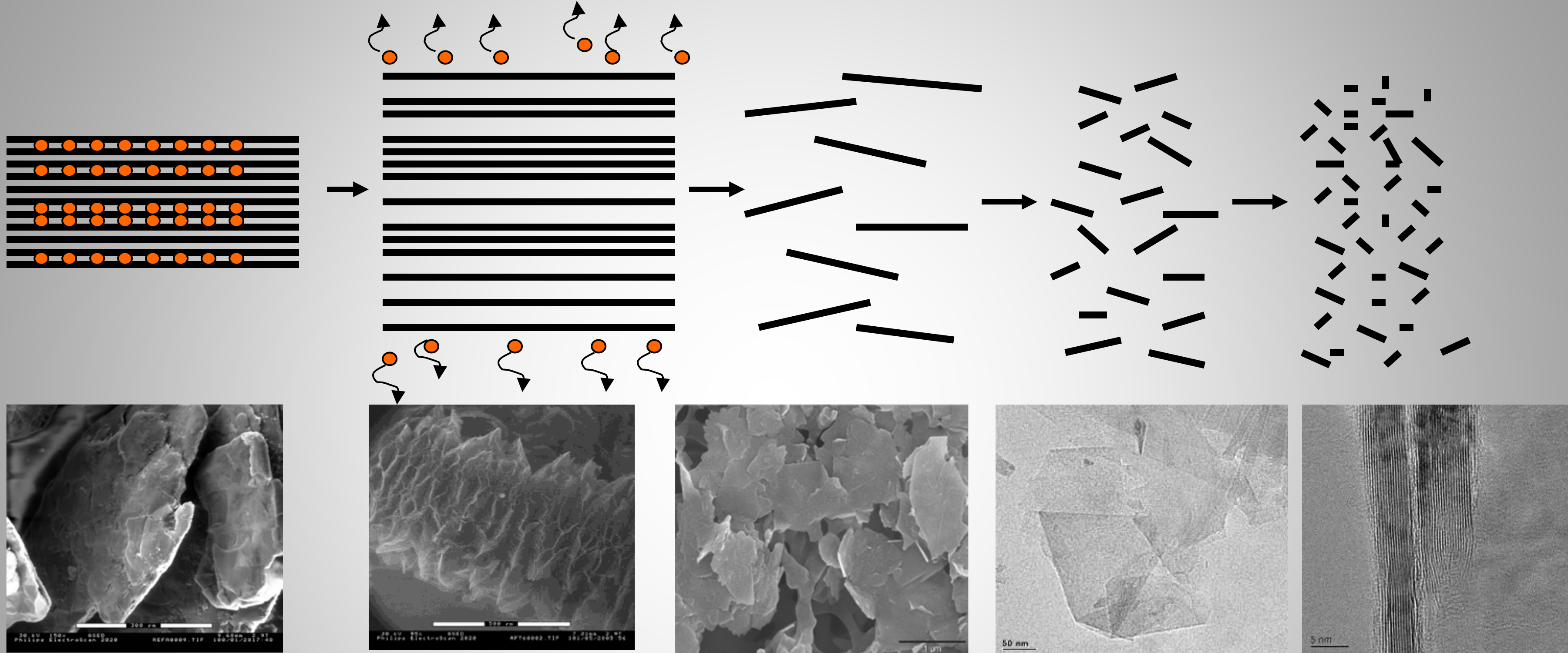
xGnP 'Ex-Situ' Exfoliation and Size Reduction



Intercalated Graphite (300-500 um)

Expanded Graphite (300-500 um)

xGnP Graphene (50-100 um)

xGnP Graphene (15 um)

xGnP Graphene (1 um)

Stacks of 10-20 lamellae are less affected by out-of-plane bending forces and retain their platelet structure during processing.

Bousmina, *Macromolecules*, 2006, *39* (12), pp 4259–4263

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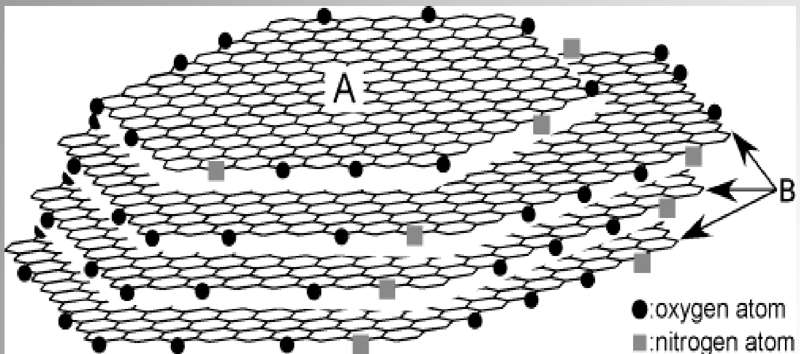
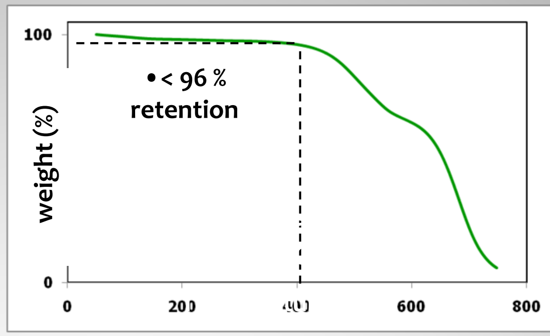
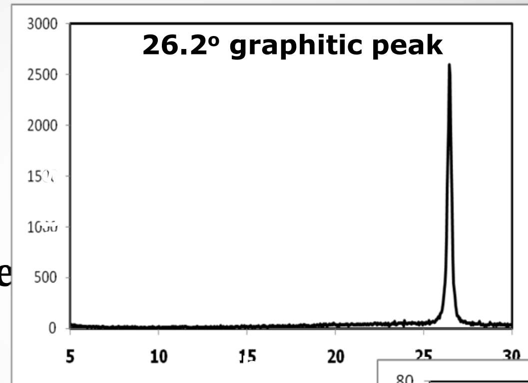
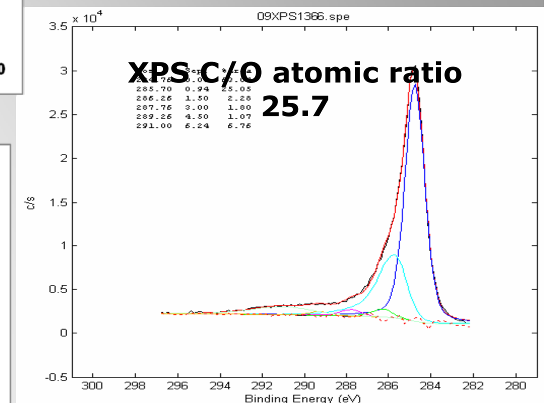
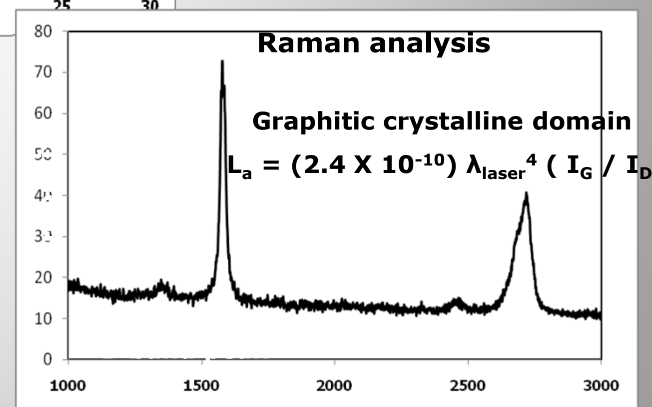
Quality of xGnP











- Layers can be intercalated and exfoliated into platelets with high aspect ratios (dia. ~0.3μ to 50μ and t.~ 1nm to 5nm)
- Basal Plane is hydrophobic
- Functional groups at xGnP edges
- Covalent bonds at edge sites
- Surface areas from 100m²/g to 750m²/g
- Some reduction in properties from monolayer graphene

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Mixing and Dispersion of xGnP

Translation of xGnP properties into applications requires dispersion and random orientation to produce isotropic properties

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Dispersion of xGnP into Polymers

- ***Water***
  - ***Coatings, Paints, Inks***
- ***Oils***
  - ***Lubrication***
- ***Thermoset Resin***
  - ***Epoxy, PU, Vinyl Ester***
- ***Thermoplastic resin***
  - ***PP, PE, Nylons***

- **Chemical Functionalization of Graphene Nanoplatelet edges**

  Plasma, Acid, Amine, Ozone
- **Surfactants**

  Anionic (SDS, SDBS, GAENPE)

  Cationic (DTAB)

  Non-Ionic (Triton)
- **Polyelectrolytes**

  PAA, PEI, PDAC, ma-PS, PVP

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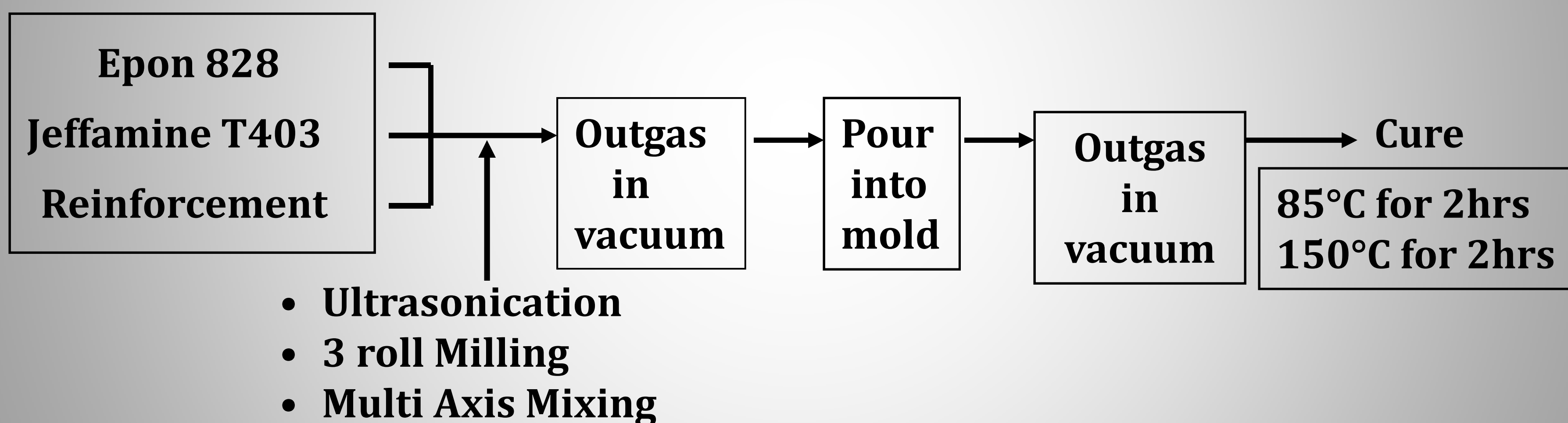
Mixing & Dispersion –(Random xGnP) Nanocomposites

Thermoset NanoComposite Fabrication



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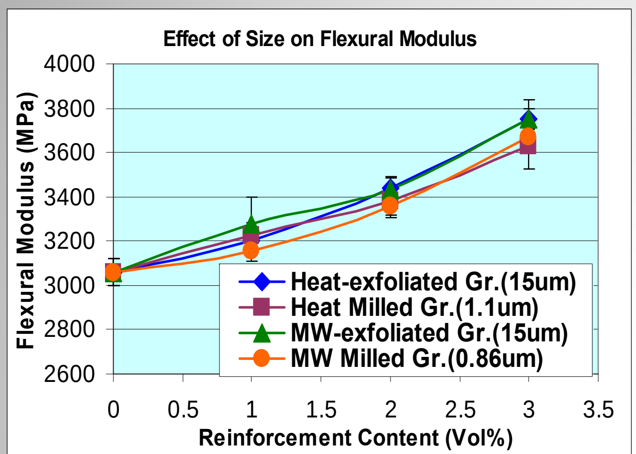
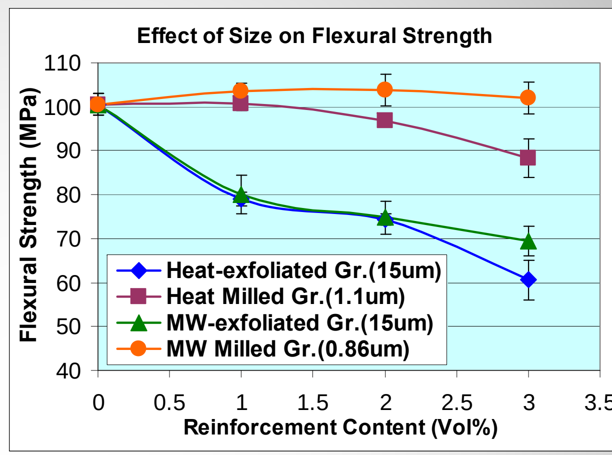
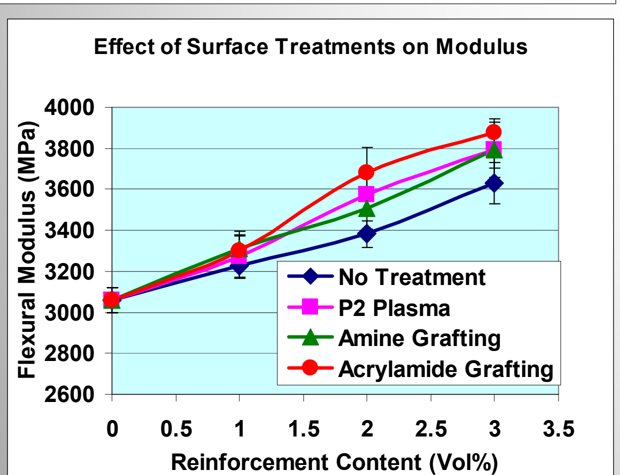
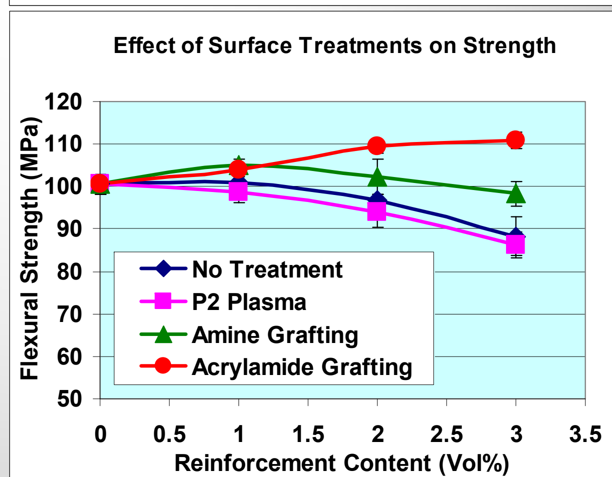
Epoxy Nanocomposite Flexural Properties: Size and Surface Chemistry of xGnP





~100m^2/g xGnP





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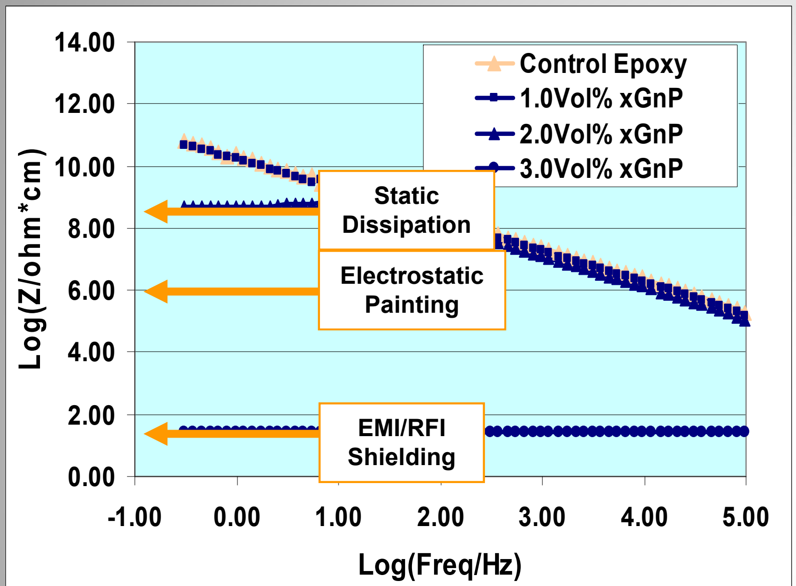
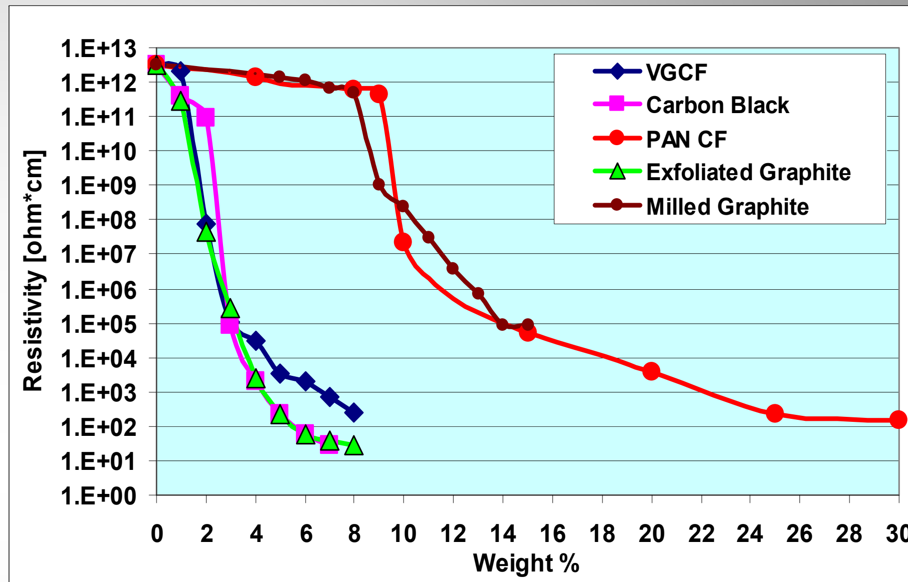
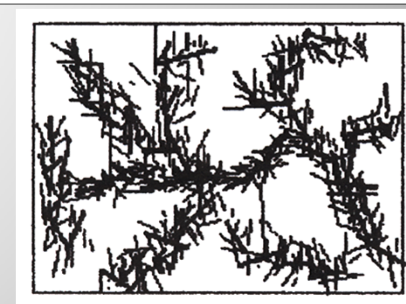
xGnP + Epoxy Electrical Resistivity







~100m²/g xGnP

Percolation Analysis

$$\rho_{eff} = \rho_0 (p - p_c)^{-t}$$

Reinforcement	pc (Vol%)	pc (Wt%)	ρ_0 (ohm*cm)	t
CF	5.90	9.76	0.4	3.26
VGCF	1.09	1.87	0.03	3.03
Carbon Black	1.29	2.00	0.01	3.03
Exfoliated Gr.	1.13	1.93	0.001	3.12

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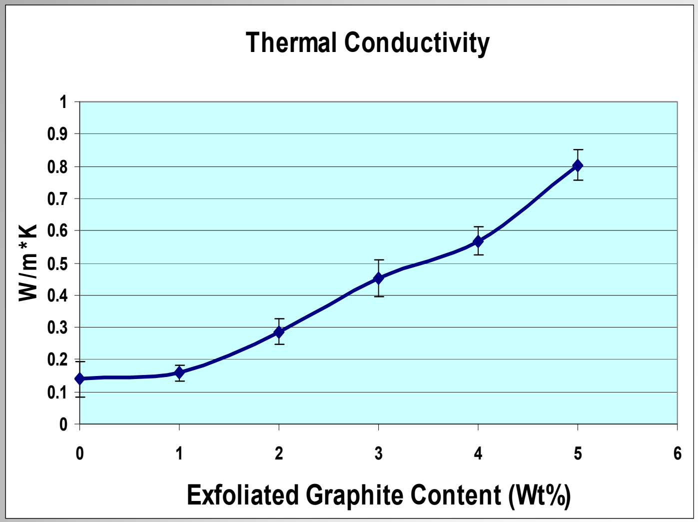
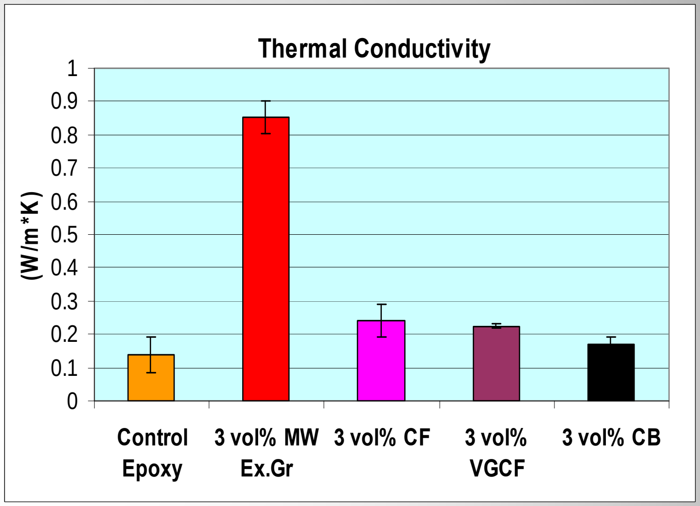
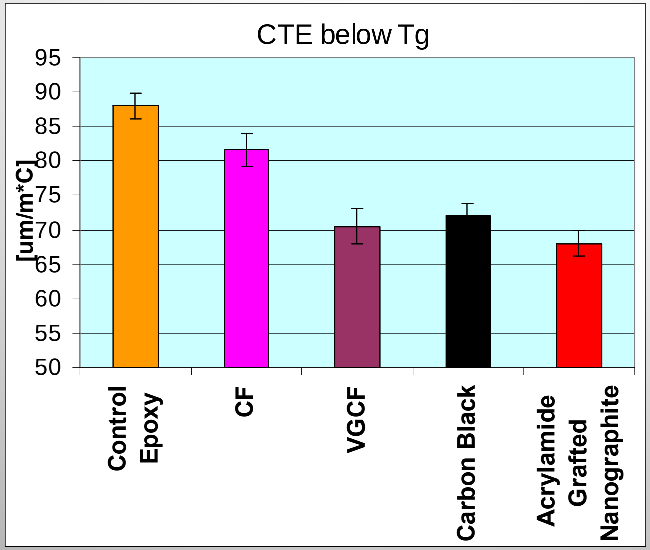
xGnP + Epoxy Thermal Conductivity and CTE





~100m^2/g xGnP



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Thermoset NanoComposite Fabrication

Epon 828 / Jeffamine T403 / Reinforcement → Outgas in vacuum → Pour into mold → Outgas in vacuum → Cure

Ultrasonicate & Mix

Cure: 85°C for 2hrs, 150°C for 2hrs

Thermoplastic NanoComposite Fabrication

Extr/InjMold

xGnP, TP → Extrude → Injection Mold

PreMix

xGnP, TP Powder → Coat Powder → Compression Mold

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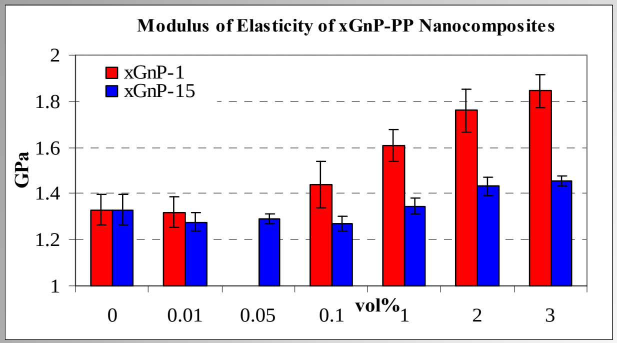
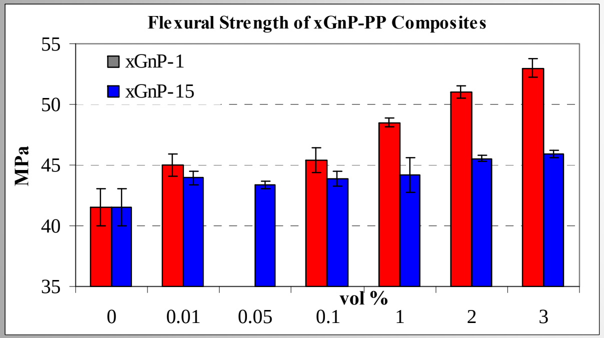
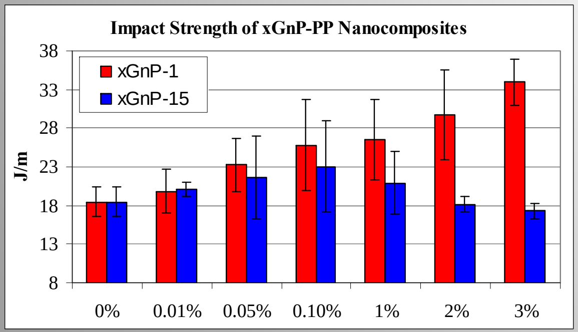
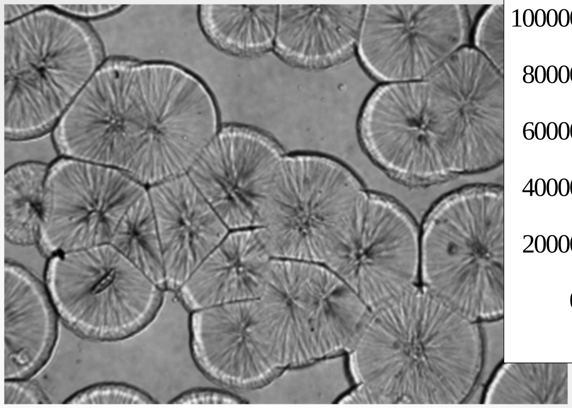
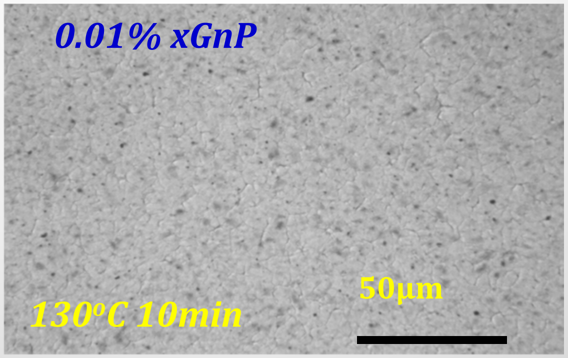
Flexural and Impact Properties of xGnP/PP

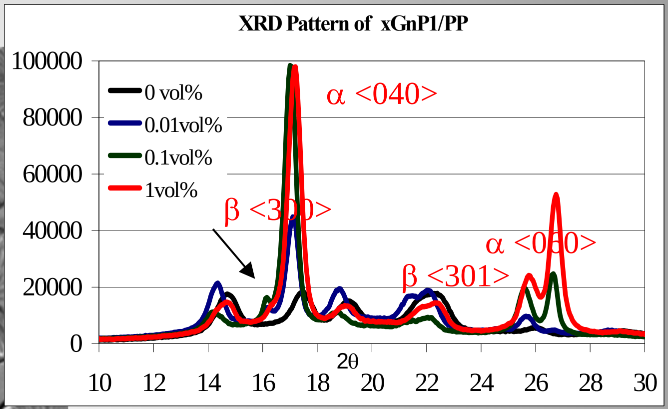












* xGnP promotes the formation of β phase crystals (at low %)

* β-phase crystals of PP have higher impact strength and toughness

* No change in the degree of crystallinity

* Tc increases by 10-20 °C (1 to 10vol% of xGnP)

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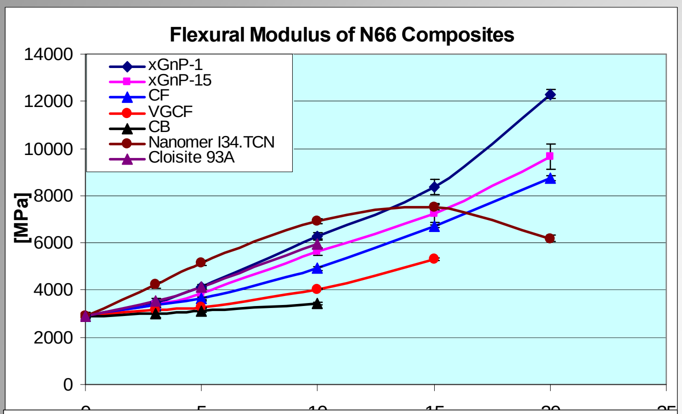
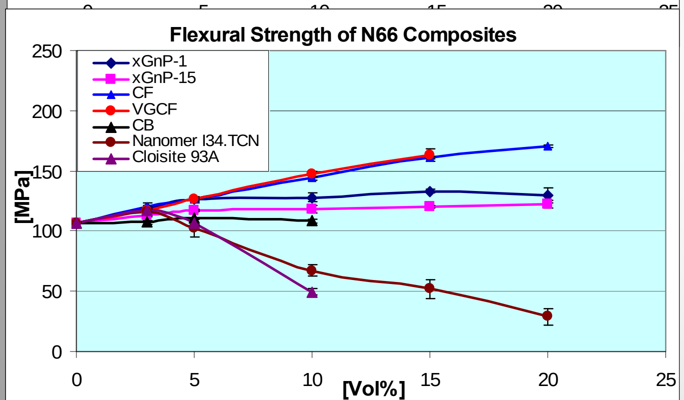
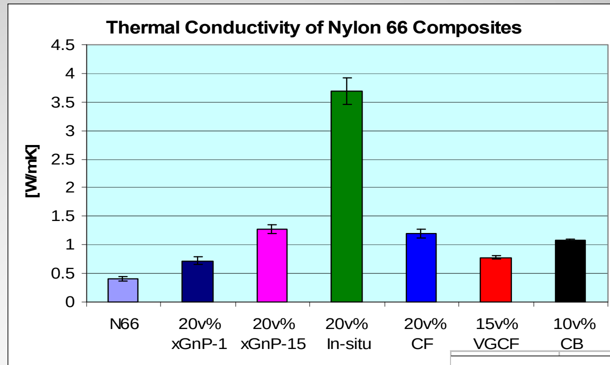
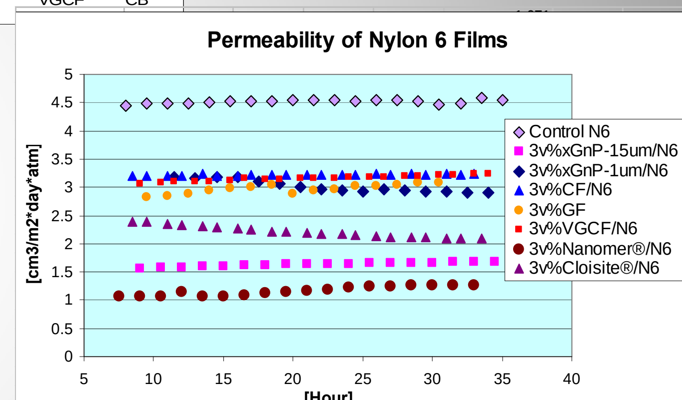
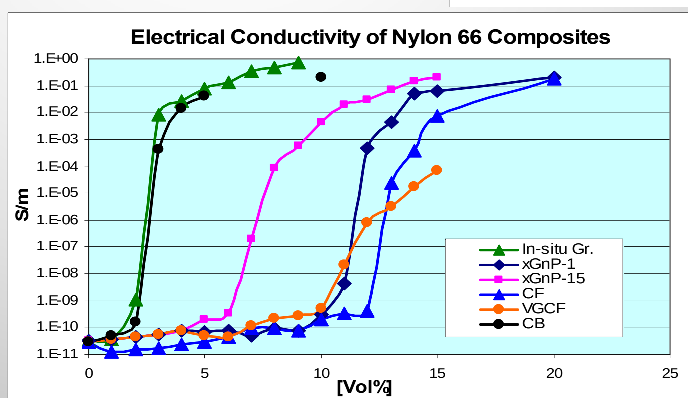
xGnP-Nylon 6 & Nylon 66 Nanocomposites











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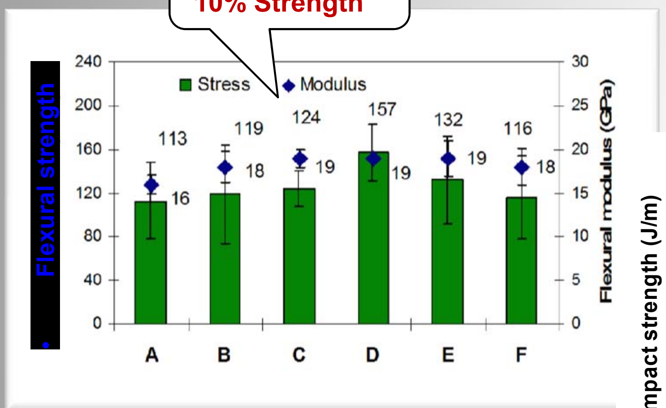
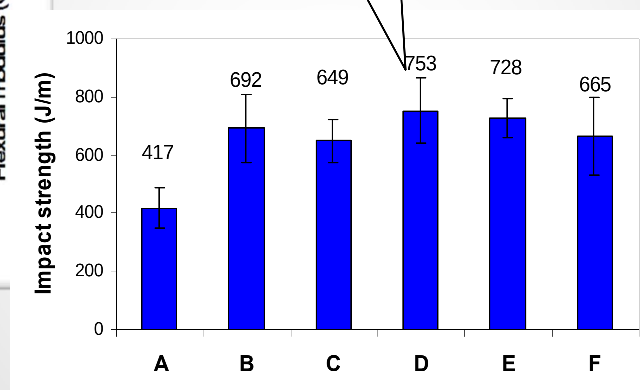
Multifunctional xGnP Modified SMC

Apply xGnP to fibers and filler with a sizing → **Mix fibers and filler with UPE** → **Add Initiator and Promoter Ultrasonicate** → **Cast and Cure**

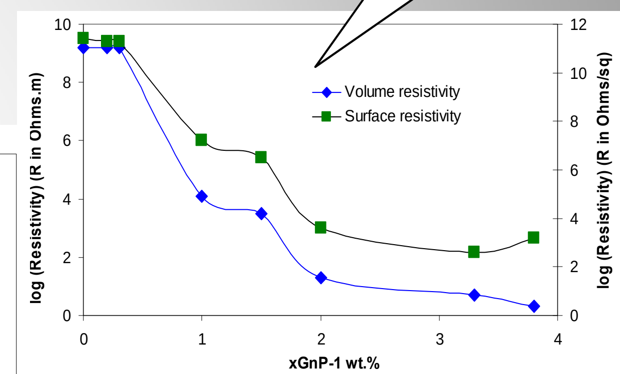
20% Modulus
10% Strength



80% Impact



10^9 increase conductivity



28%(glass fiber) + 47% ($CaCO_3$) + 3%(UPE)

A= (xGnP 0%)

B= (xGnP 0.3%)

C= (xGnP 1.0%)

D= (xGnP 1.5%)

E= (xGnP 2.0%)

F= (xGnP 3.8%)

D= 28% (glass fiber) + 47% ($CaCO_3$ /3.2% xGnP-1)

+23%(UPE)= composite (xGnP™ 1.5%)

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Nano-Structuring

Assembling individual xGnP particles into 1D, 2D and 3D Morphologies to enhance desirable properties

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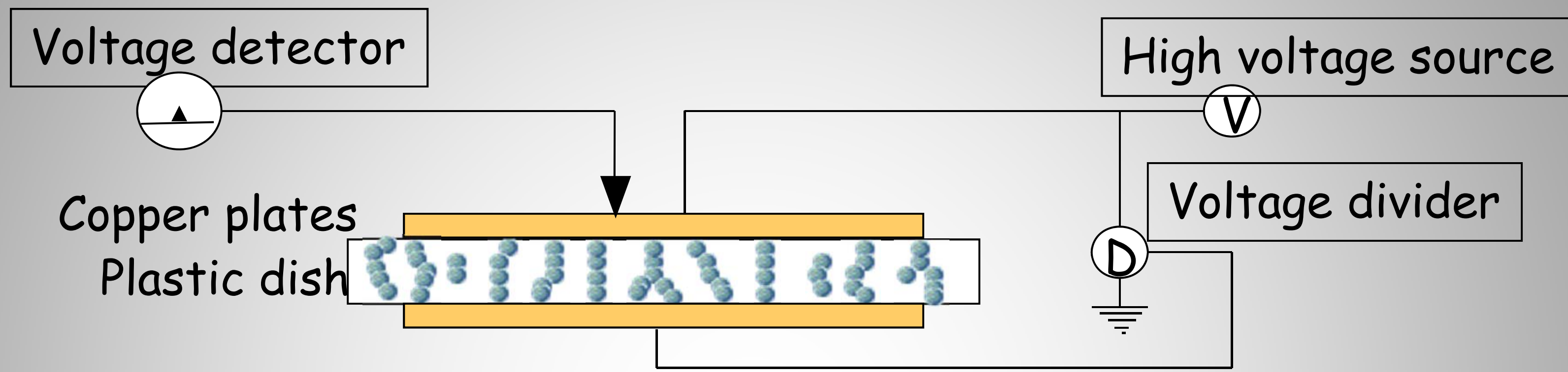
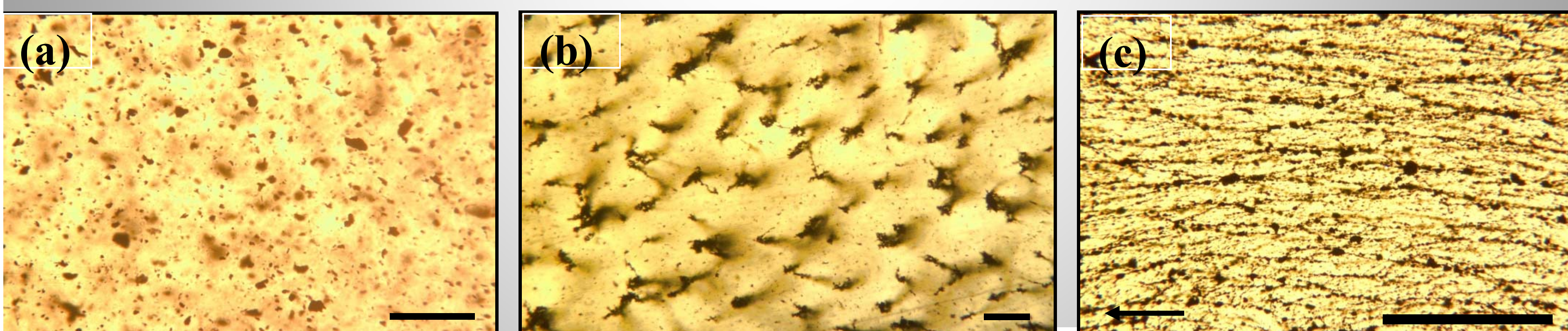
1-D Morphology   E-Field Alignment



E field Intensity: ~10-25KV/cm



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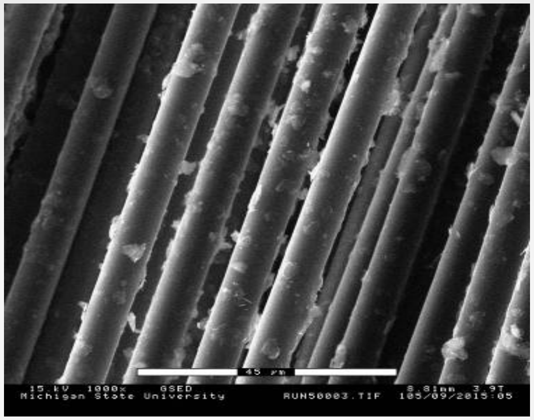
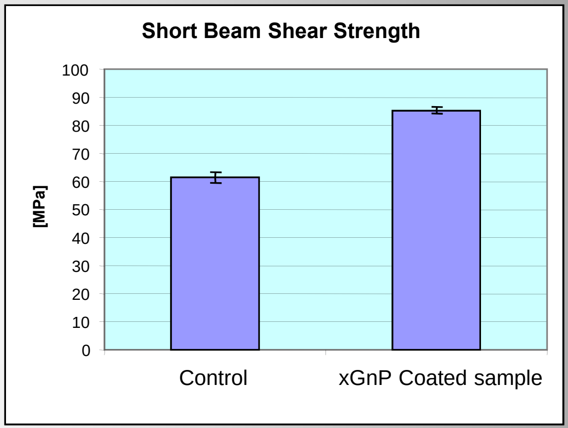
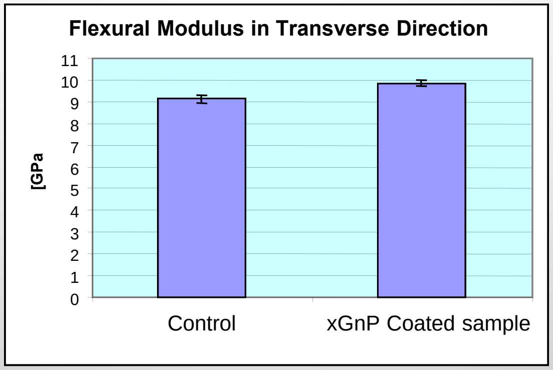
1D Nano-Structuring xGnP on Fiber Surfaces to Enhance Transverse Properties

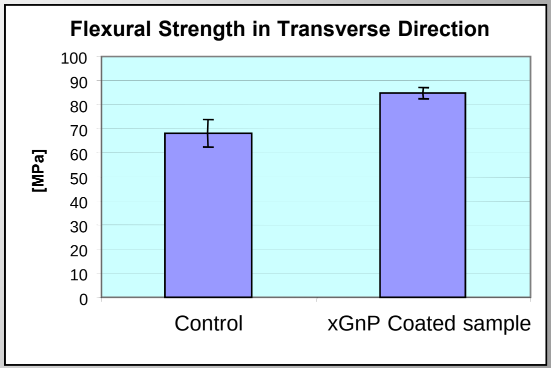
xGnP Sized Fiber

- **Interfacial Adhesion**
- **Transverse**
- **Energy Absorption**
- **Conductivity**
- **Any Fiber**
- **Standard Process**









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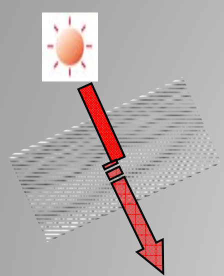
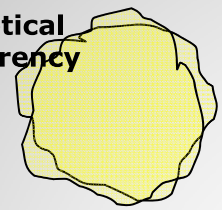
2D - Transparent Conductive Monolayer xGnP

A single layer graphene absorbs 2.3% of visible light



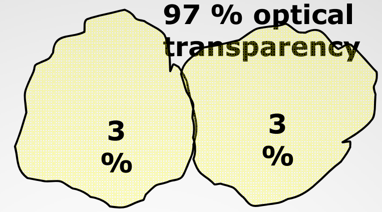
94% optical transparency



Stacking graphene nanosheets

linear decrease in optical transparency

97 % optical transparency



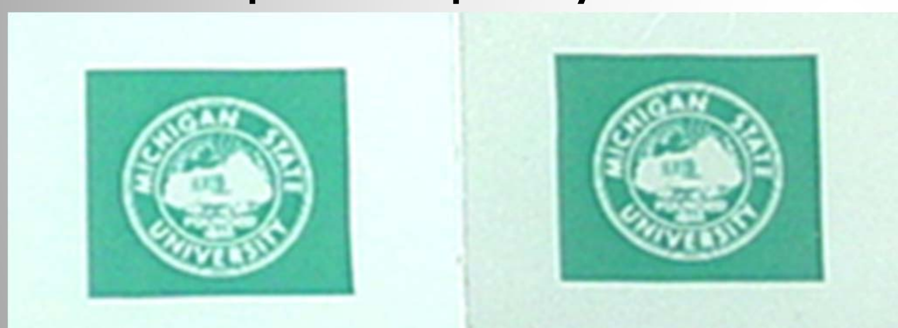
Edge shared network of xGnP by liquid-liquid self-assembly

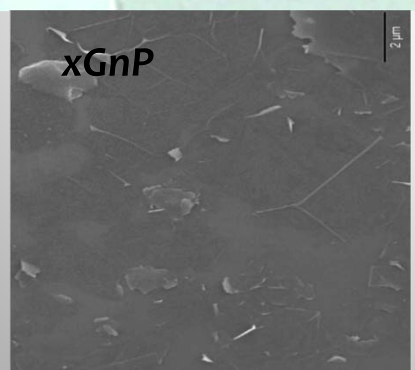
Advantages

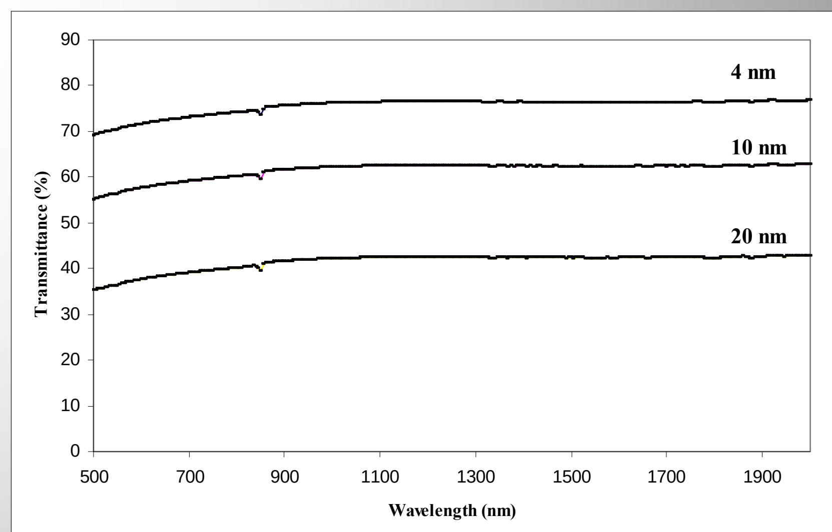
~80% Transparent from 500 nm – 2000 nm

1000+ S/cm

Simple to Produce







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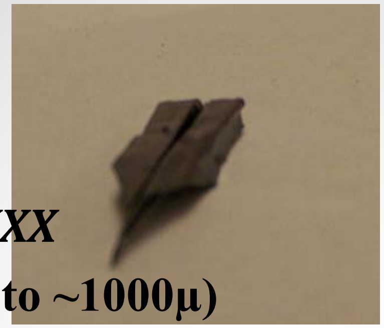
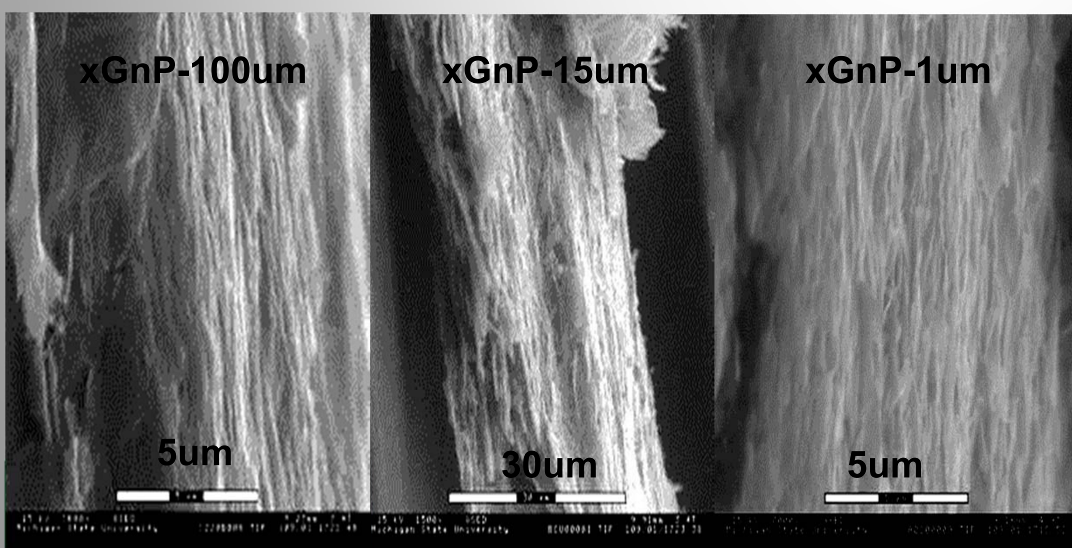
Biswas and Drzal, NanoLetters, 9, 167-172, 2009

2D Multilayer xGnP 'Paper'

Superior Electrical and Thermal Conductivity



- Highly Aligned xGnP
- Controllable size 35 cm x *XXX*
- Controllable thickness (~3µ to ~1000µ)
- Simple process
- Scalable to large sheets 2m+ *XXX*



- *Electrical conductivity: 2128 S/cm*
  Surface resistivity: 0.1 ohm/sq
  OFHC Copper: $5.8*10^5$ S/cm
- *xGnP paper density ~2g/cm^3*
  Cu density ~8.9 g/cm^3
- *Thermal Conductivity*
  ~ 200 W/m^{o}K -in-plane
  ~ 5 W/m^{o}K –thru-plane
  Cu is ~ 400 W/m^{o}K

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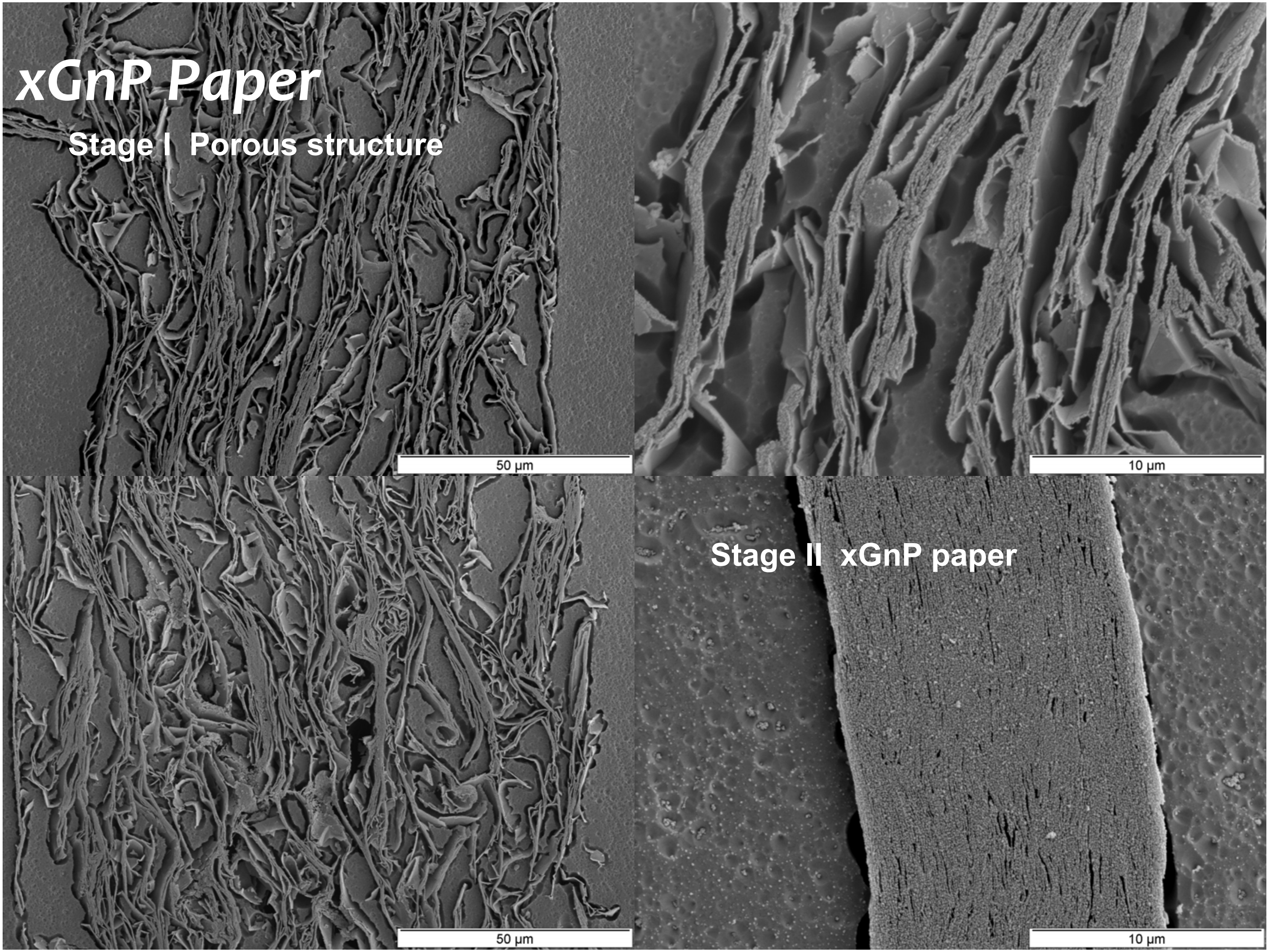
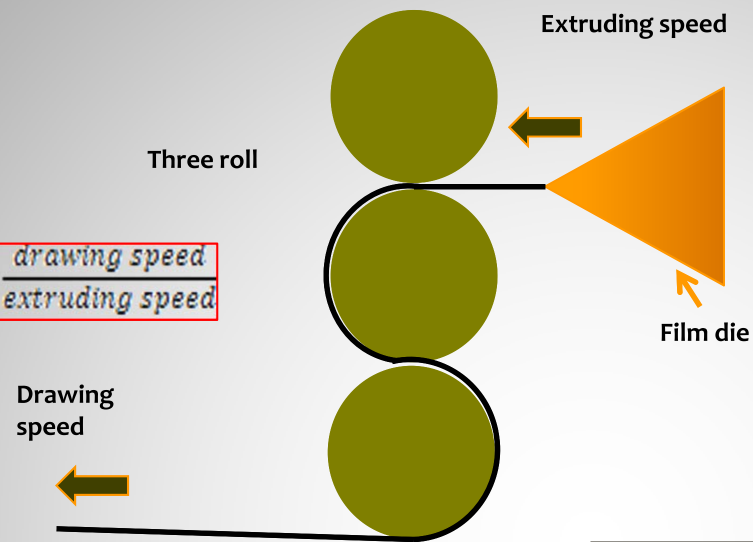

xGnP Paper
Stage I Porous structure
50 μm
10 μm
50 μm
Stage II xGnP paper
10 μm

Continuously Extruded xGnP-5/PEId film

$$\text{stretching ratio} = \frac{\text{drawing speed}}{\text{extruding speed}}$$



Purpose: investigate the possibility of fabricating layered composite with xGnP/PEId film

Material: extrusion cast film

- 10wt% xGnP-5/PEId composite film, stretching ratio=2, 0.3mm thickness, 16 layers
- Neat PEId film, stretching ratio=3, 0.22mm thickness, 15 layers

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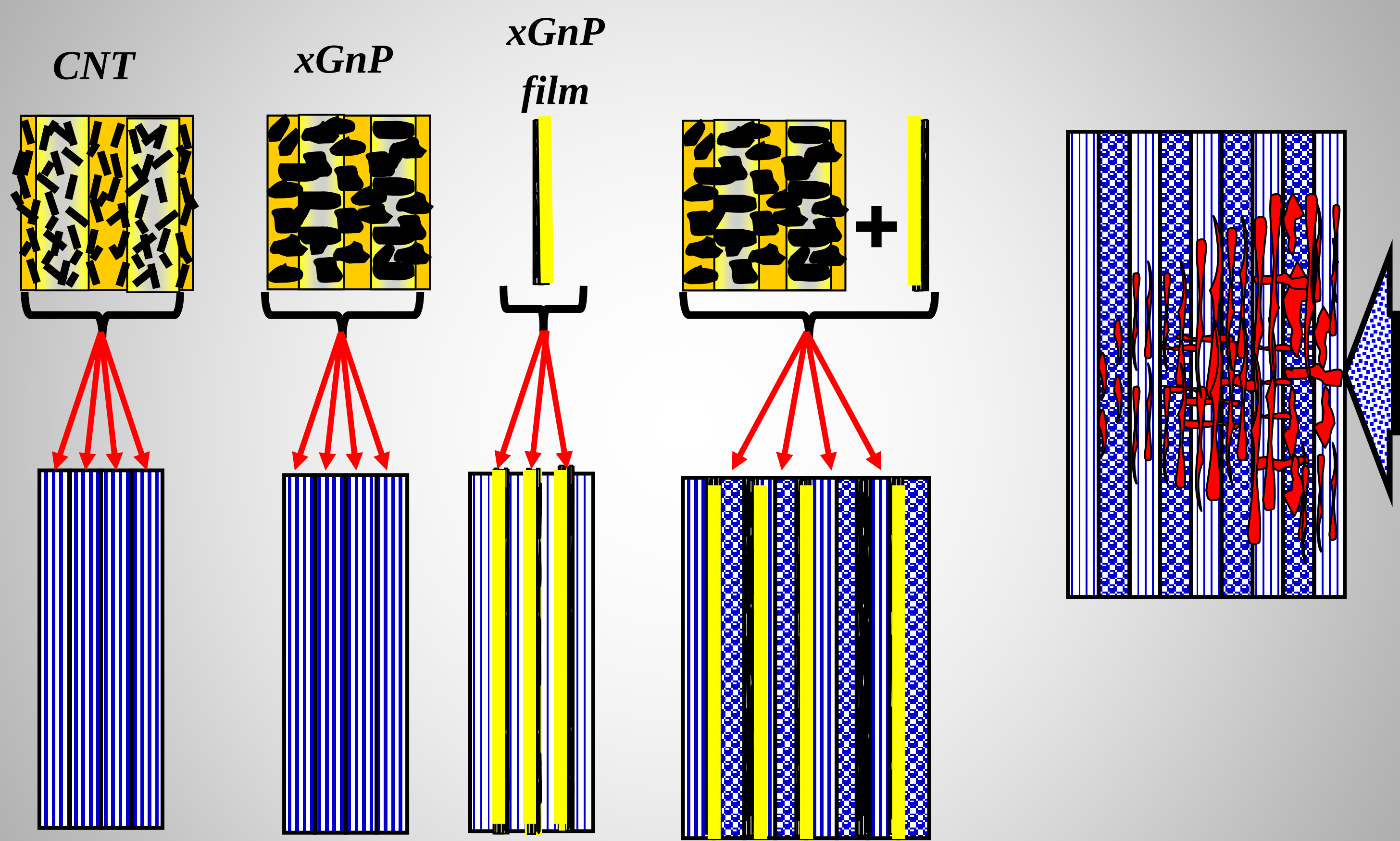
Composite Fiber-Matrix Interphase xGnP Modification: Intra and Interlaminar



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xGnP Paper Properties

	Loading & xGnP type	Modulus (GPa)	Strength (MPa)	Electrical conductivity (S/cm)*	Thermal conductivity (W/m°K)*	Relative O_2 Permeability
Injection molding xGnP+PEI	10wt% xGnP-5	6.6	98	E-6.7		
	Annealed			E-3.0		
Compression molding xGnP+PEI	10wt% xGnP-5	5.7	98	E-4.5	0.40	
SSBM & Pre-coating xGnP+PEI	5wt% xGnP-15	3.9	65	1.25	0.85 (t- plane, 3.3 @ 10wt%)	
Extrusion cast xGnP-PEI film	10wt% xGnP-5	6.8	106	E-6.1	0.29 (t-plane)	0.35
	Annealed			E-4.3	0.80	
Pressed xGnP paper	xGnP-15	7.0	2.8	850	246	
	xGnP-100			2200	313	
xGnP paper -PEI	80wt% xGnP-15	19	23	620		
xGnP paper -PEI	70wt% xGnP-15	22	32	550		0.01
xGnP paper - epoxy	15wt% xGnP-15				20.5	0.02

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xGnP for Energy Generation and Storage

- **Supercapacitors**
  - **Hybridize xGnP**
- **Li Ion Batteries**
  - **Nano-structure for faster transport, stress relief**
- **BiPolar Plates in PEM Fuel Cells**
  - **Mechanical , Thermal and Electrical Metrics**
- **Transparent Electrodes for Dye Sensitized Solar Cells**
  - **Replace ITO**
- **Efficient Solar Phase Change Heat Storage Materials**

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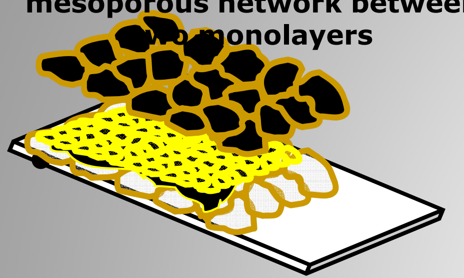
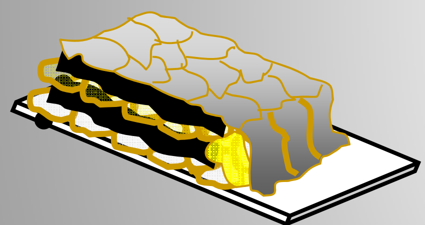
3D Morphology - Supercapacitor Electrode from Hybrid Variable Sized xGnP

Small xGnP to form mesoporous network between two monolayers



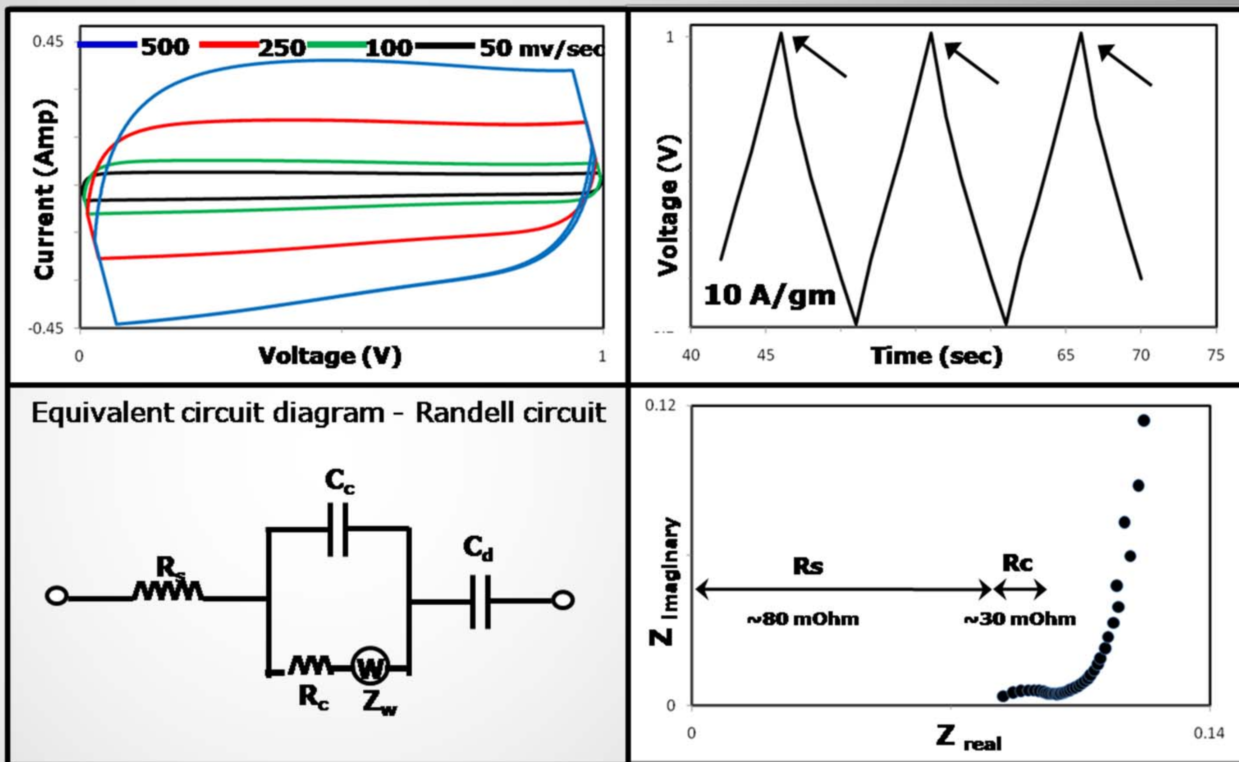
Multilayer deposition of large and small xGnP



Multilayer electrode of variable size xGnP

Cyclic voltammetry (CV)

Charge discharge behavior



Complex plane impedance analysis

Electrolyte ~ 6M KOH in water

Capacitance: 165-250+ F/gm at 10 A/gm discharge current density

Electrode resistance: 30 mOhm, Time constant: 633 msec, Knee frequency: 150 Hz

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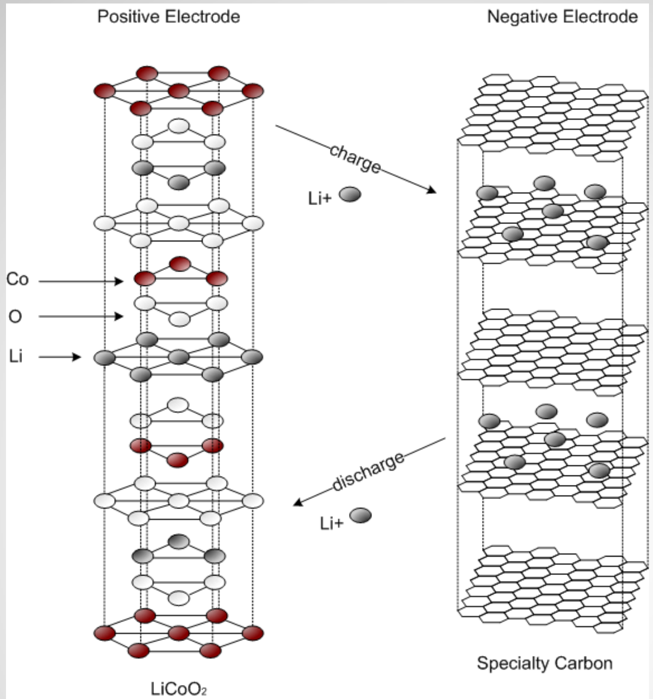
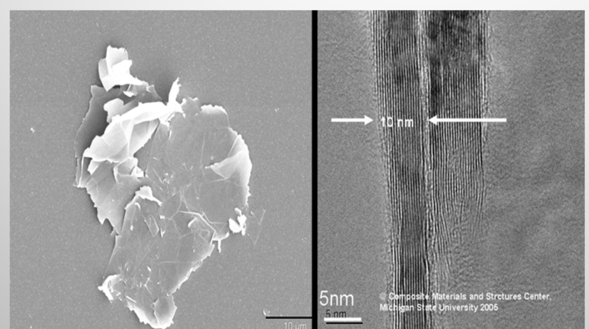
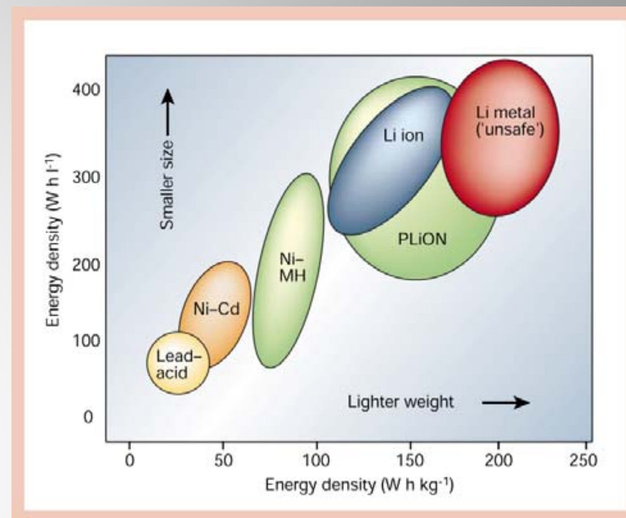
xGnP Nano-structured Lithium Ion Battery

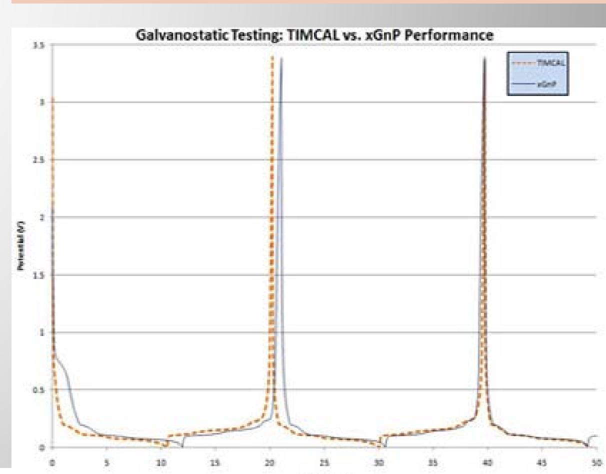
<u>**Advantages**</u>

- **High Energy Density**
- **High Power Density**
- **Greater Durability**
- **Faster Recharging**
- **Low Internal Resistance**
- **Nano-Structured xGnP for optimal Li transport**
- **Functionalize the edges of xGnP to control SEI formation and morphology**
- **Conductivity Additive for Cathode**
- **Current Collector**









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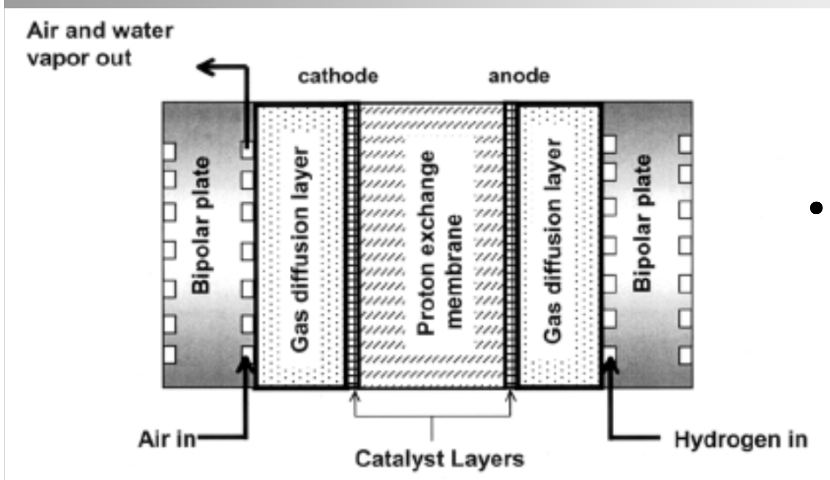
Bipolar plates in Proton Exchange Membrane (PEM) Fuel Cells



- **Bipolar plates account for approximately 80% of the fuel cell volume, 70% of the fuel cell weight and as much as 60% of the entire stack cost.**

- **Bipolar must exhibit:**
  - **in-plane electrical conductivity >100 S cm^{-1}**
  - **thermal conductivity >10W/m^{o}K**
  - **chemical stability <16mA/cm^2**
  - **gas permeability: <2×10^{-6} cm^3 (cm^2 s)$^{-1}$**
  - **mechanical strength: flexural strength > 25MPa**

- **xGnP + Thermoplastic Matrix has an excellent chance to achieve the desired DOE metrics if xGnP can be dispersed at a high level**

Ref: Journal of Power Sources. 2003;114(1):32-53

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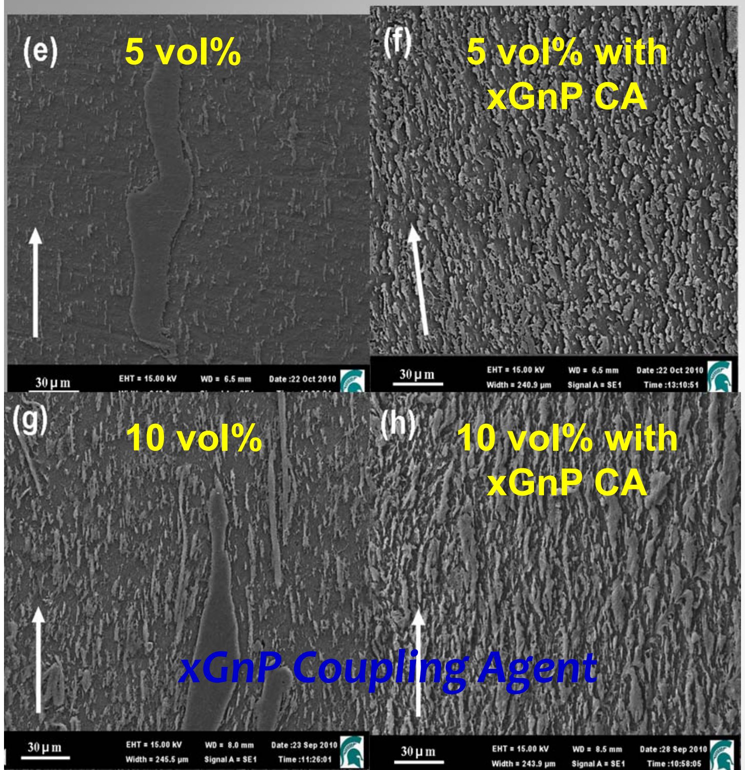
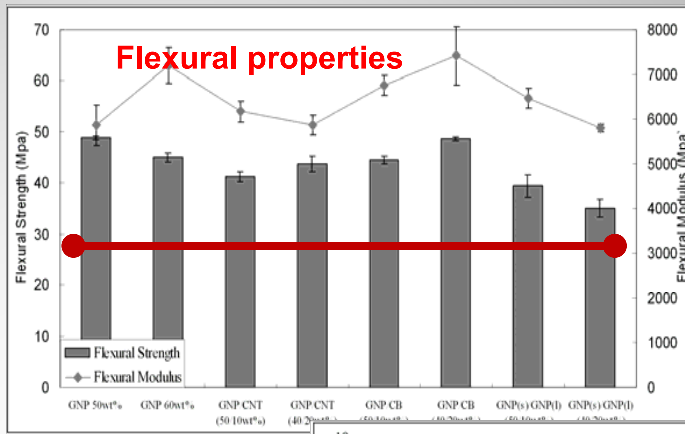
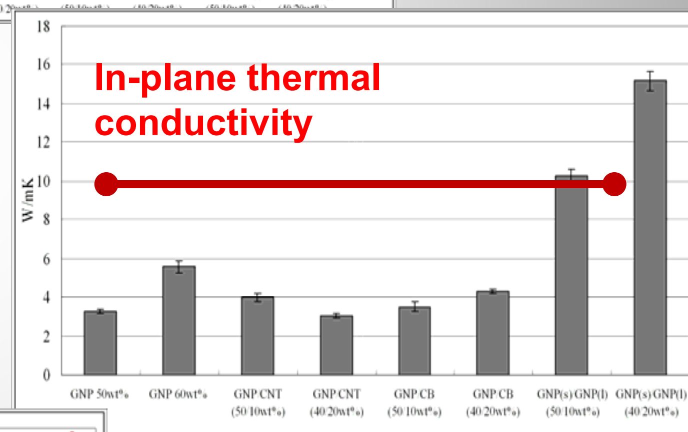
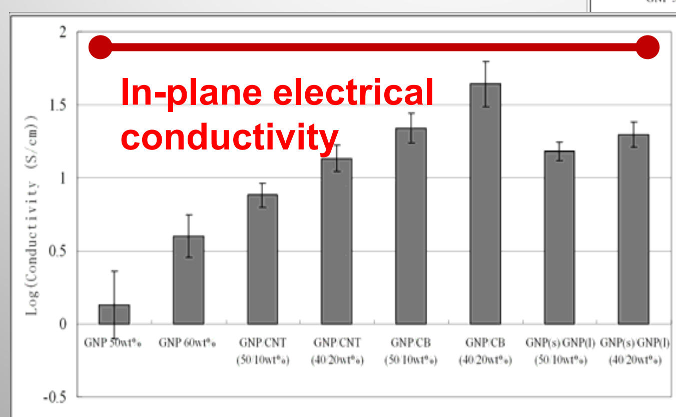
xGnP-HDPE Bipolar Plates









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Summary: xGnP Multifunctional Nano- Material

- **Multifunctional Graphene Nanoplatelet :**
  - **xGnP can be produced by multiple synthesis routes**
  - **Direct Intercalation/Exfoliation to produce platelet morphology**
    - **Platelet Thickness; Diameter ; Surface and Edge Chemistry; Metal/metal oxide coating**
    - **Dispersible in water, solvent and thermoset and thermoplastic polymers**
  - **xGnP multifunctional properties**
    - **High Modulus, Low Density**
    - **High Electrical Conductivity**
    - **High Thermal Conductivity**
    - **Optically Transparency**
    - **Thermo-Oxidative Resistance**
    - **Barrier Properties**
    - **Electrochemically and Thermally Stable**
    - **Cost Effective**
- **Potential Applications for xGnP:**
  - **Dispersible in Polymers and Water, Variable size**
  - **Nano-Engineered for Controlled (1D, 2D or 3D) Morphology**
  - **Transformational Material for Multifunctional Lightweight Composites, Alternative Energy Generation and Storage Devices**

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