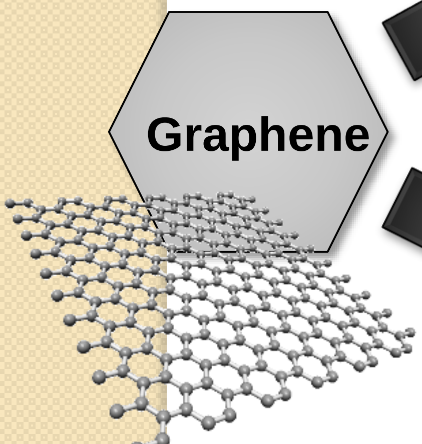
UNIVERSITI TEKNOLOGI MALAYSIA

Graphene Malaysia 2016
8- 9th Nov 2016

Marriage of Graphene and Cellulose for Reinforced Composite Preparation

Zaiton Abdul Majid, Wan Hazman Danial and Mohd Bakri Bakar



Unique properties

Graphene Synthesis

Graphene Characterization

Sensor

Composites

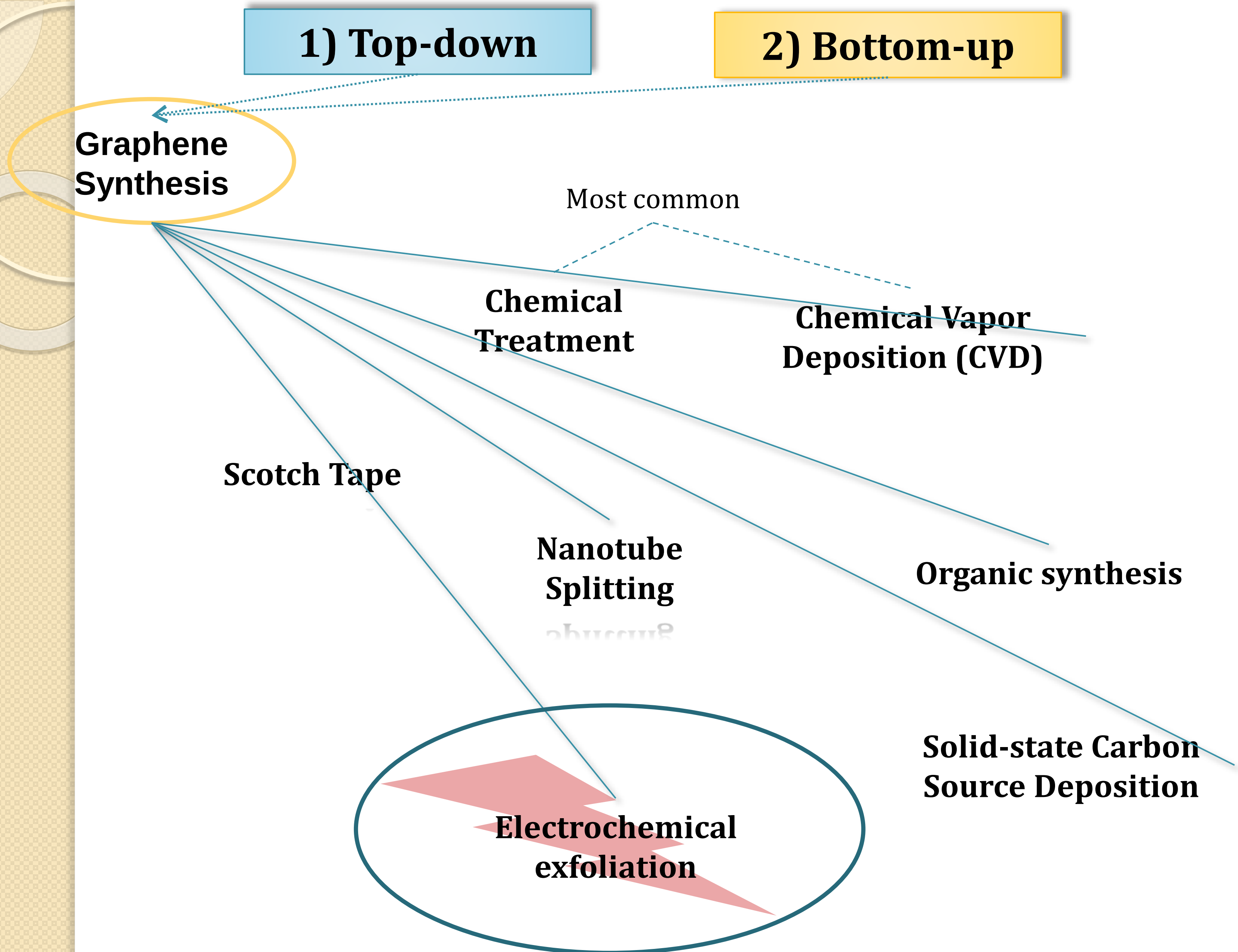
Conductive film

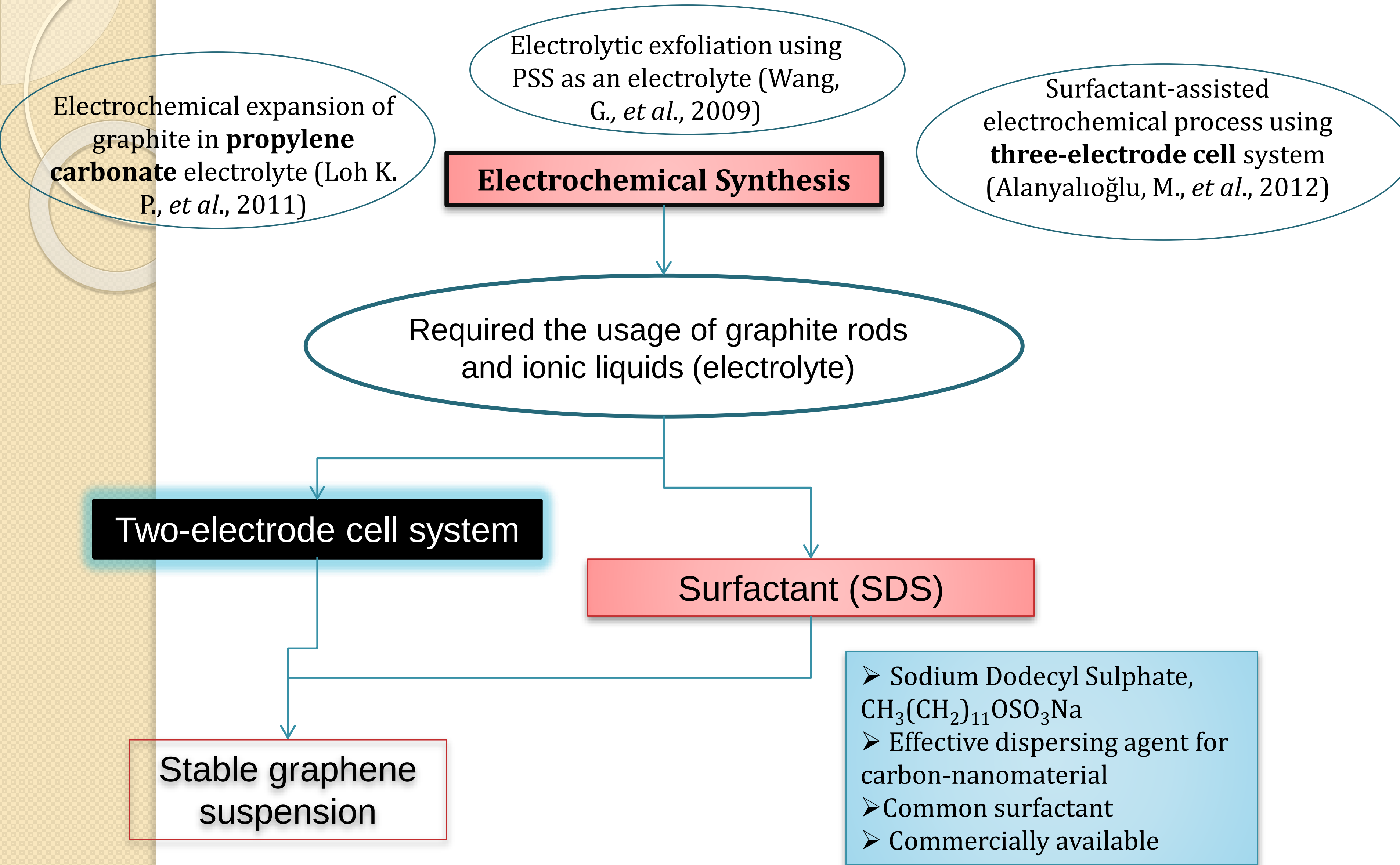
Nanoelectronics

Solar cells

Fuel cells

Reinforcing material

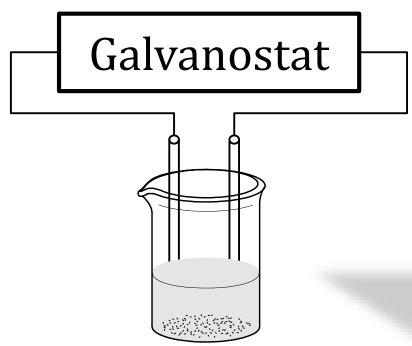

1) Top-down
2) Bottom-up
Graphene Synthesis
Most common
Chemical Treatment
Chemical Vapor Deposition (CVD)
Scotch Tape
Nanotube Splitting
Organic synthesis
Solid-state Carbon Source Deposition
Electrochemical exfoliation


Electrochemical expansion of graphite in **propylene carbonate** electrolyte (Loh K. P., *et al*., 2011)
Electrolytic exfoliation using PSS as an electrolyte (Wang, G., *et al*., 2009)
Surfactant-assisted electrochemical process using **three-electrode cell** system (Alanyalıoğlu, M., *et al*., 2012)
Electrochemical Synthesis
Required the usage of graphite rods and ionic liquids (electrolyte)
Two-electrode cell system
Surfactant (SDS)
Stable graphene suspension
➢ Sodium Dodecyl Sulphate, $CH_3(CH_2)_{11}OSO_3Na$
➢ Effective dispersing agent for carbon-nanomaterial
➢ Common surfactant
➢ Commercially available

EXPERIMENTAL

Electrochemical synthesis of Graphene

- Electrode
  - High purity graphite rods
    - Anode (positively charge electrode)
    - Cathode
- Constant voltage)
- Electrolyte
  - SDS (0.1 M, 0.01 M)
  - Milli-Q ultra pure water



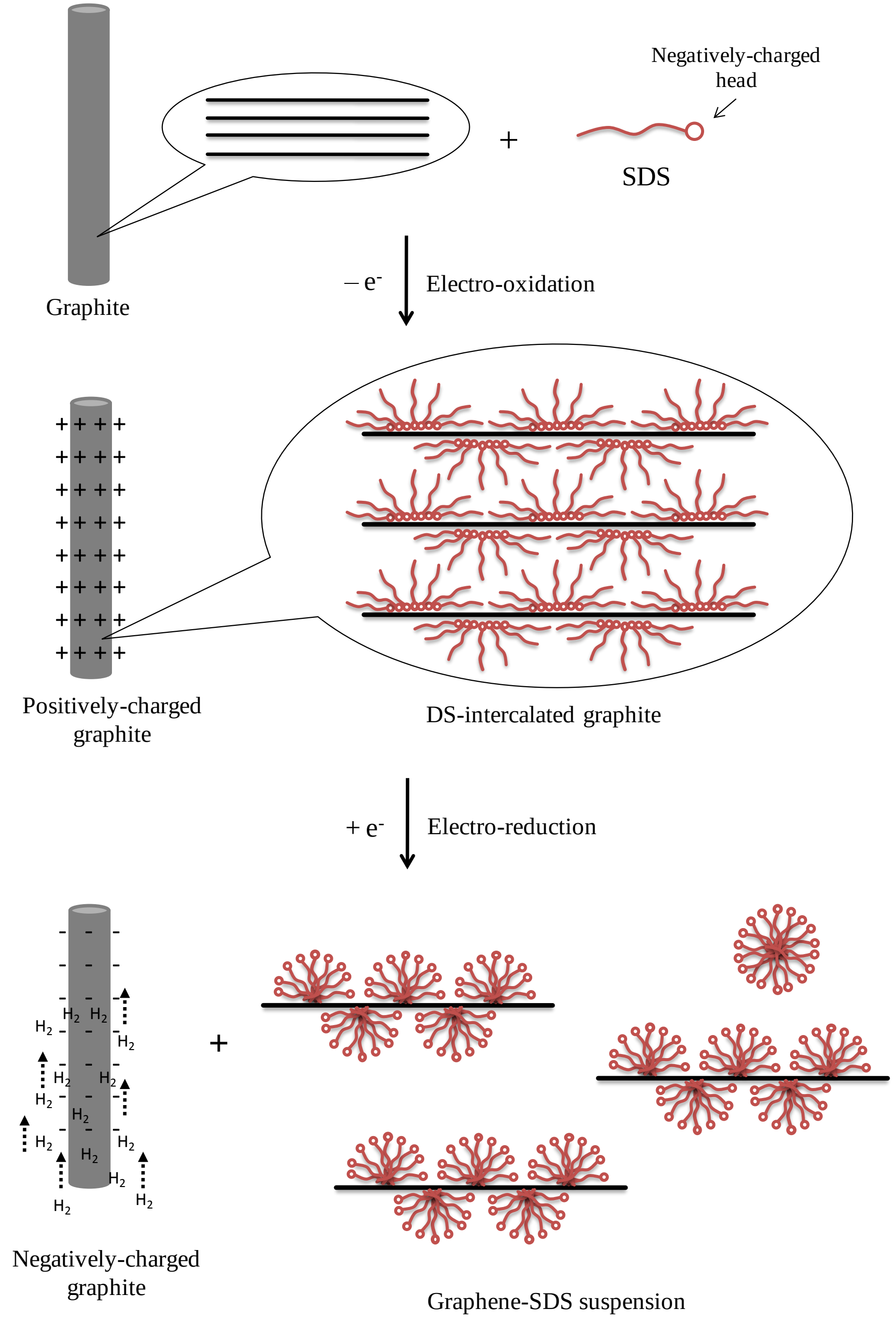
W. H. Danial *et. al*, *AIP Conf. Proc*, 1669, 020020(2015)

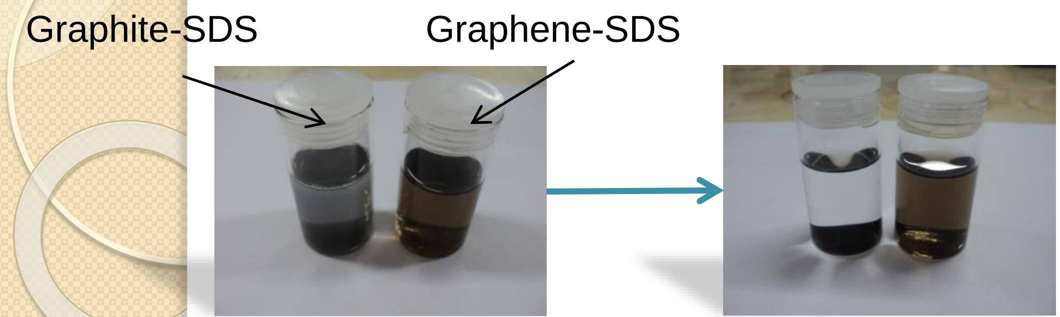
Electrochemical Synthesis of Graphene

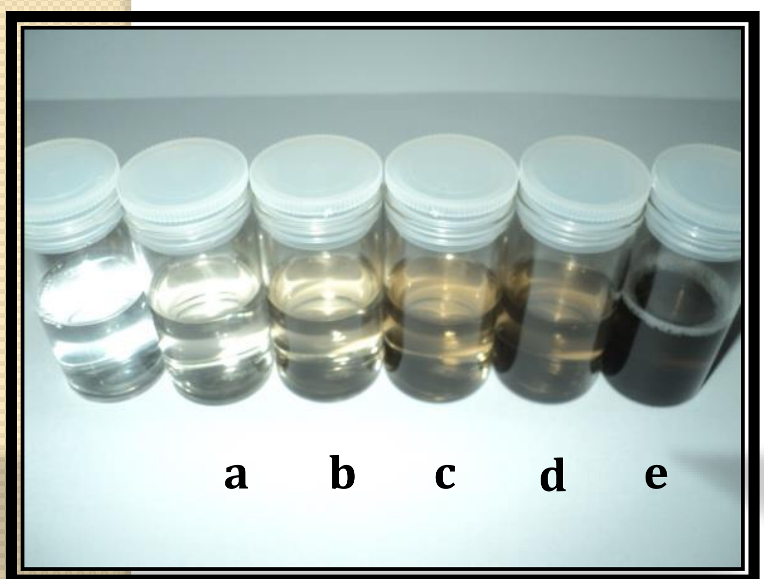
- An extremely **stable** graphene suspension was obtained
- Involve intercalation and **exfoliation** effect
- **Electric current** was used as the oxidizing & reducing agent

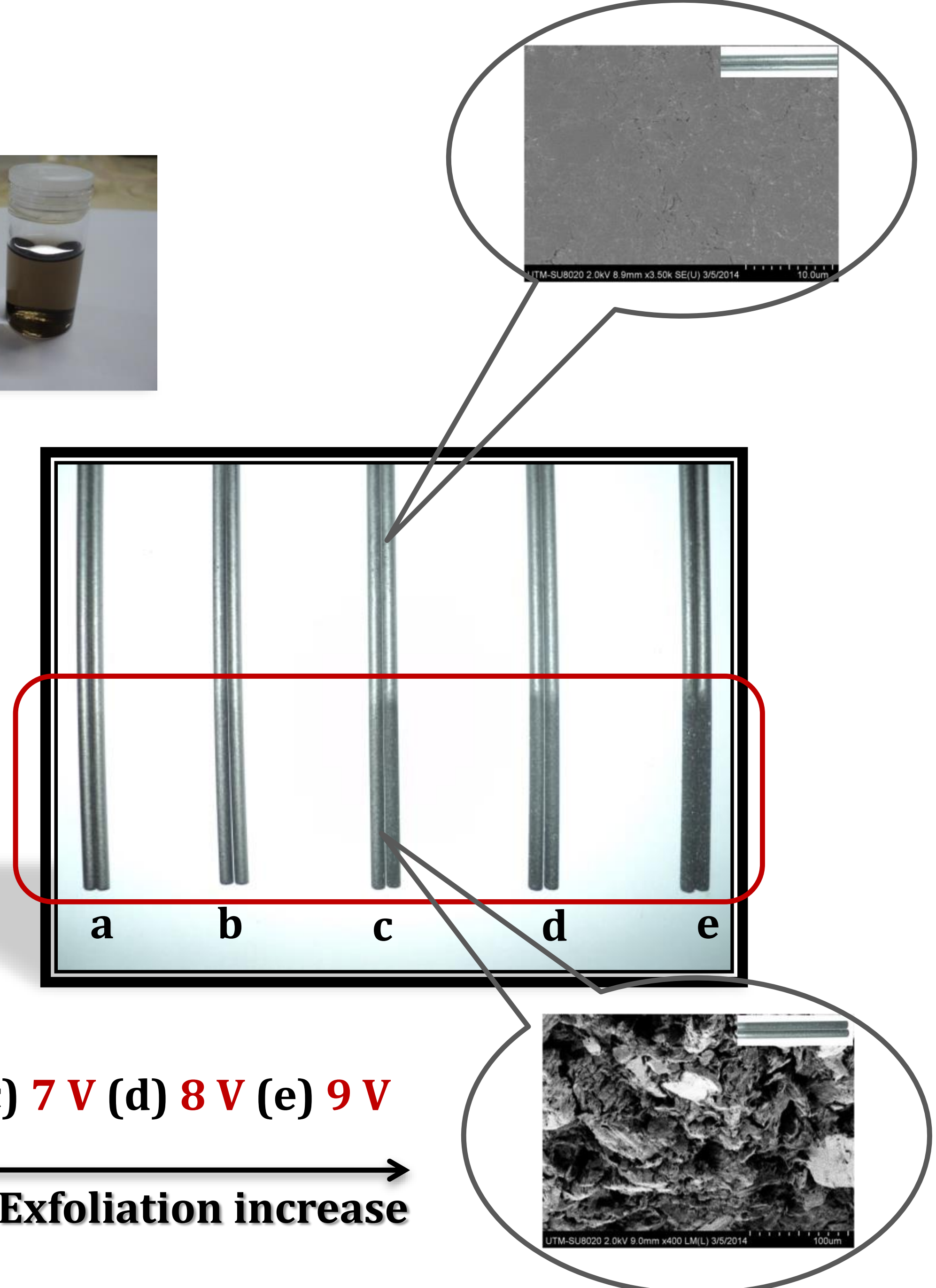
At the anode: $C_x + DS^- + H_2O \leftrightarrow (C_x^+DS^-)H_2O + e^-$

At the cathode: $H^+ + 2e^- \rightarrow H_2$ (g)







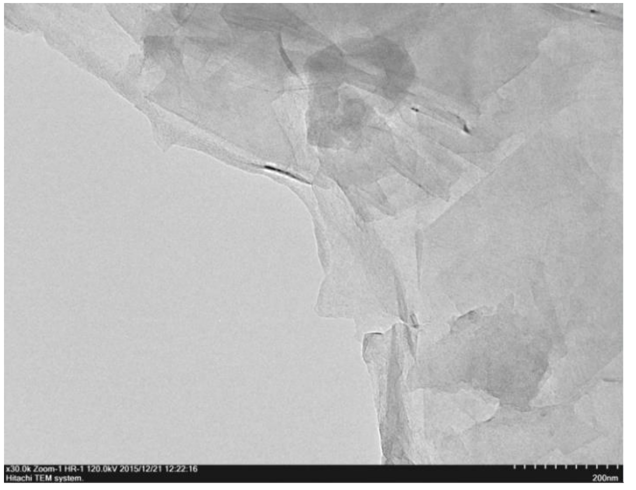


(a) 5 V (b) 6 V (c) 7 V (d) 8 V (e) 9 V

Electrochemical Exfoliation increase

TEM Images


x30.0k Zoom-1 HR-1 120.0kV 2015/12/21 12:21:07
Hitachi TEM system.
200nm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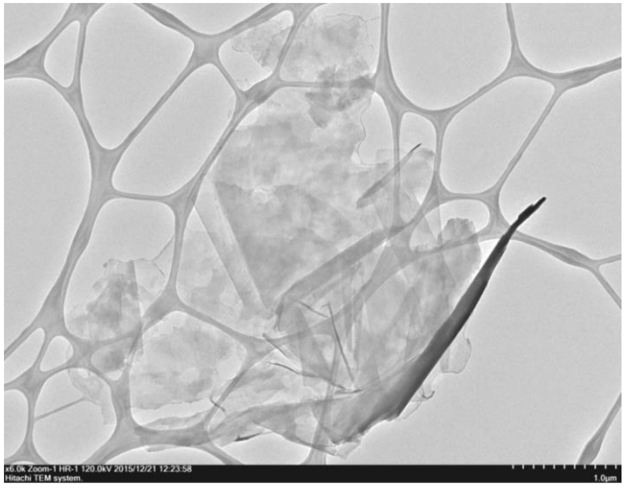
Hitachi TEM system.
200nm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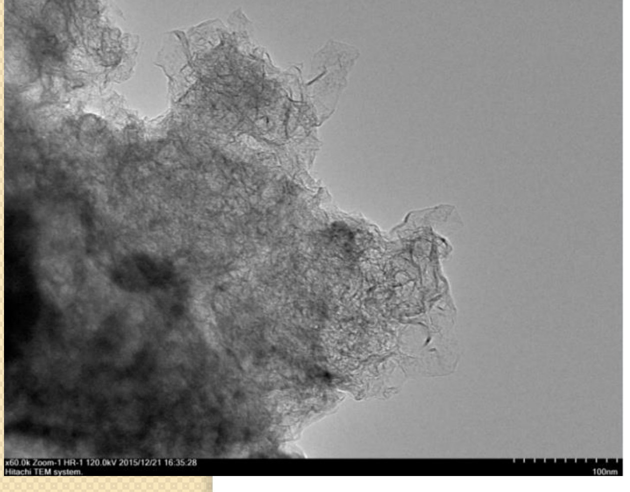
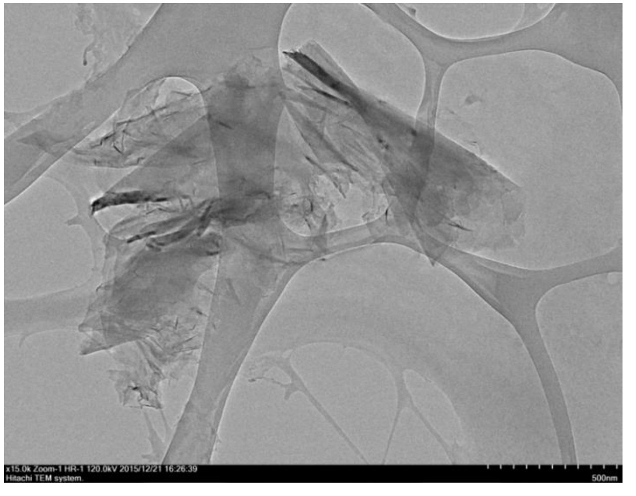
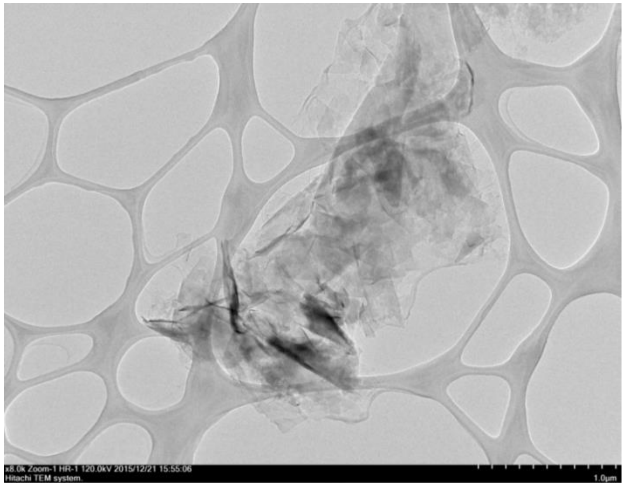
Hitachi TEM system.
1.0μm


x60.0k Zoom-1 HR-1 120.0kV 2015/12/21 16:35:28
Hitachi TEM system.
100nm


x15.0k Zoom-1 HR-1 120.0kV 2015/12/21 16:26:39
Hitachi TEM system.
500nm

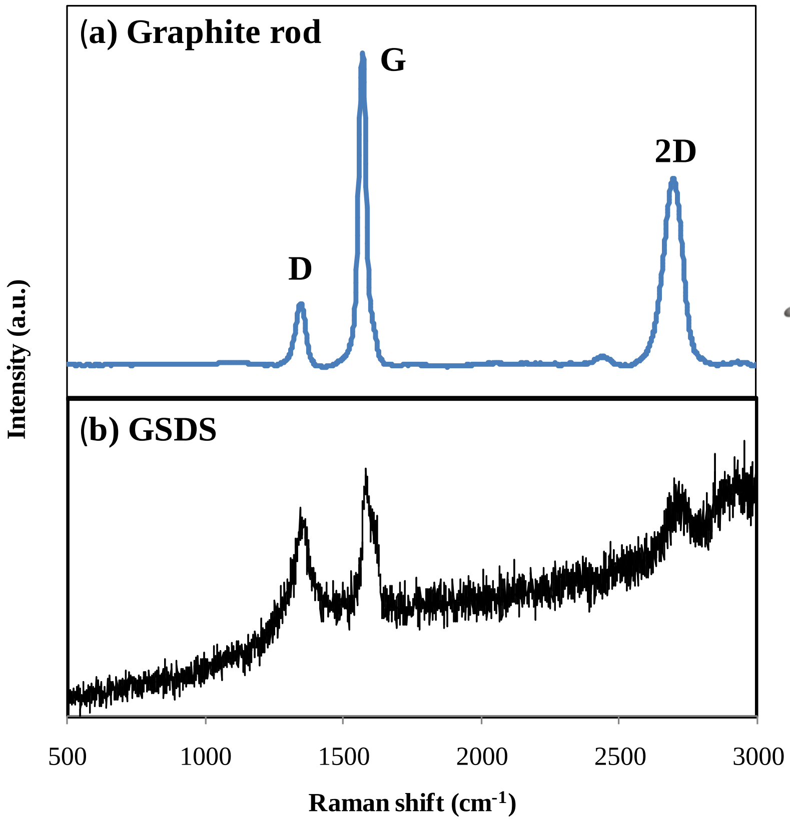

x8.0k Zoom-1 HR-1 120.0kV 2015/12/21 15:55:06
Hitachi TEM system.
1.0μm

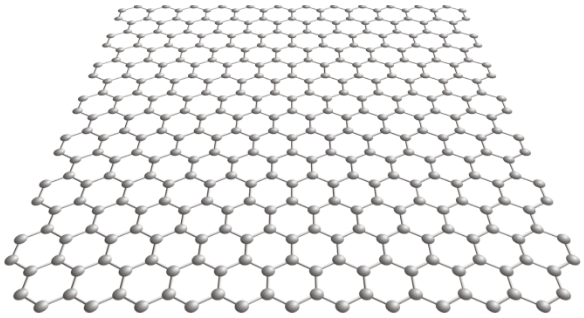
Raman Analysis

D band: 1350 cm^{-1}

G band: 1590 cm^{-1}

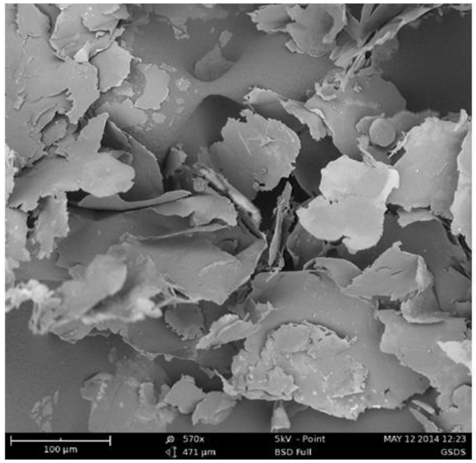
2D band: 2700 cm^{-1}

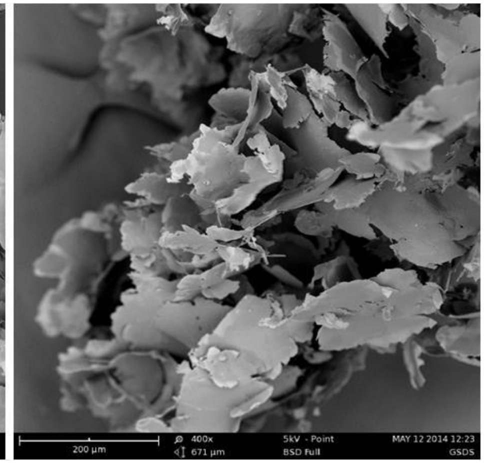




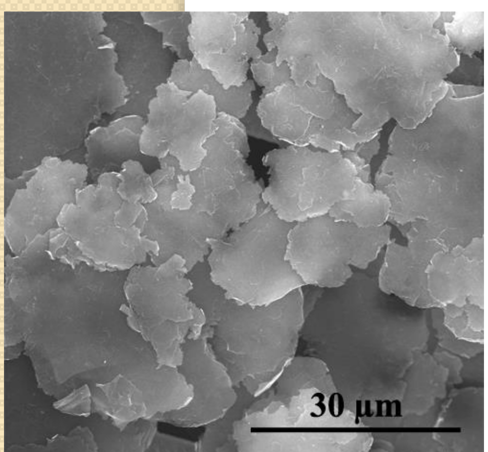
SEM Images

Electrochemical synthesized graphene platelets

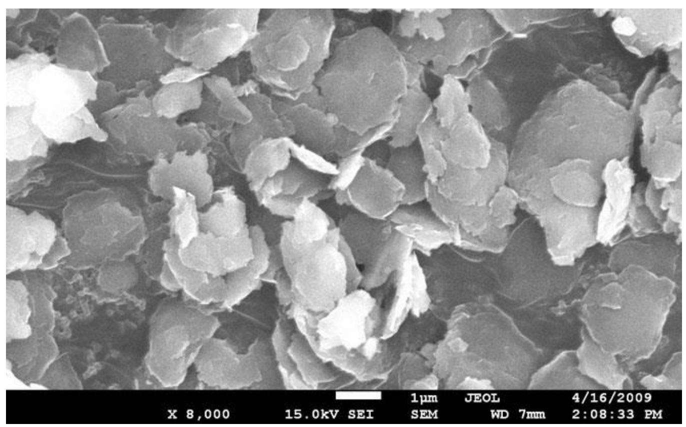




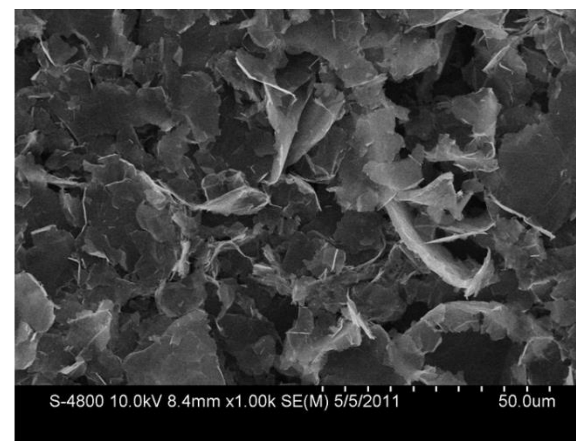
Commercialized graphene



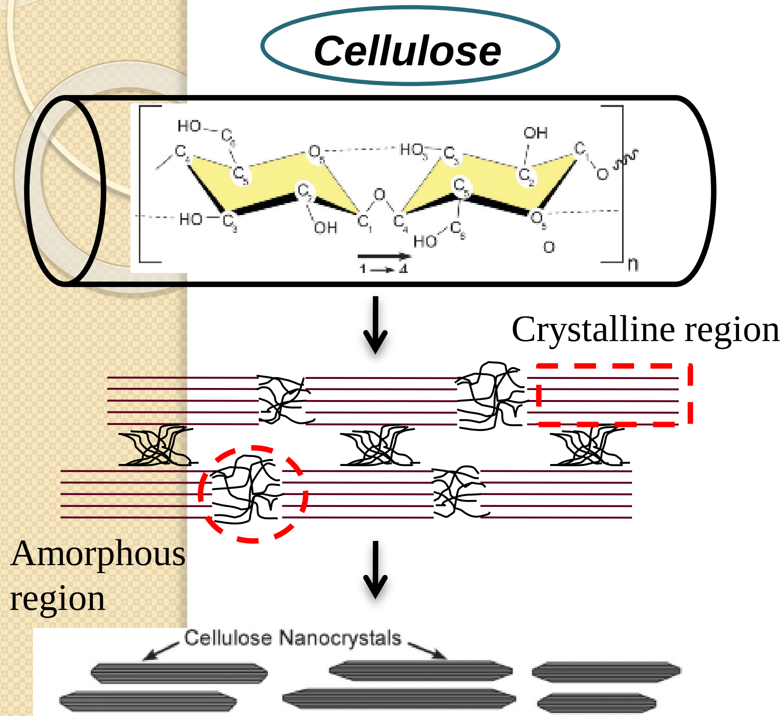
Graphene supermarket: graphene nanopowder: grade



Graphene Nanoplatelets: ACS material products

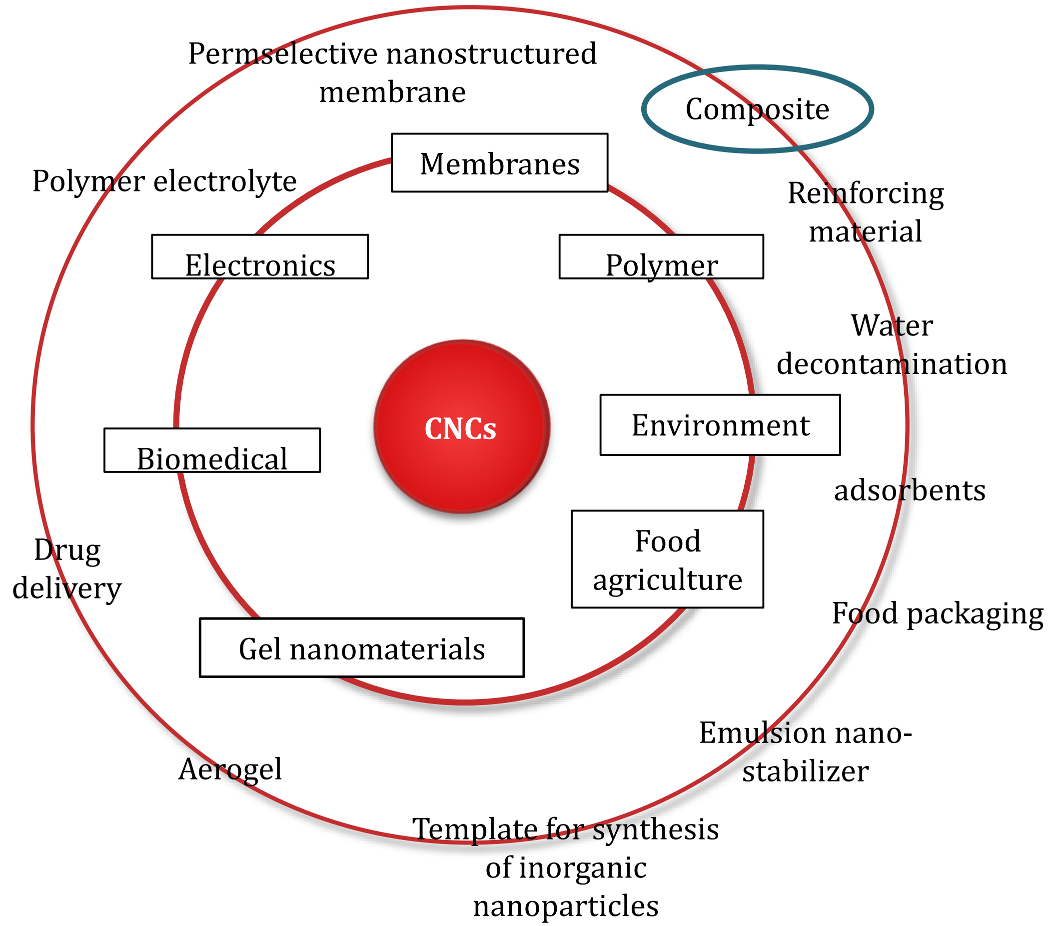


Graphene Nanoplatelets: Knano



Cellulose Nanocrystal (CNCs)

- **Highly ordered (crystalline) structure of cellulose**
- **Rod-like (l ~ 50 – 500 nm, ø ~ 3 – 5 nm, Moon *et al.* (2011))**
- **High aspect ratio**



Types of cellulose fibres

Wood and Plant Fibres

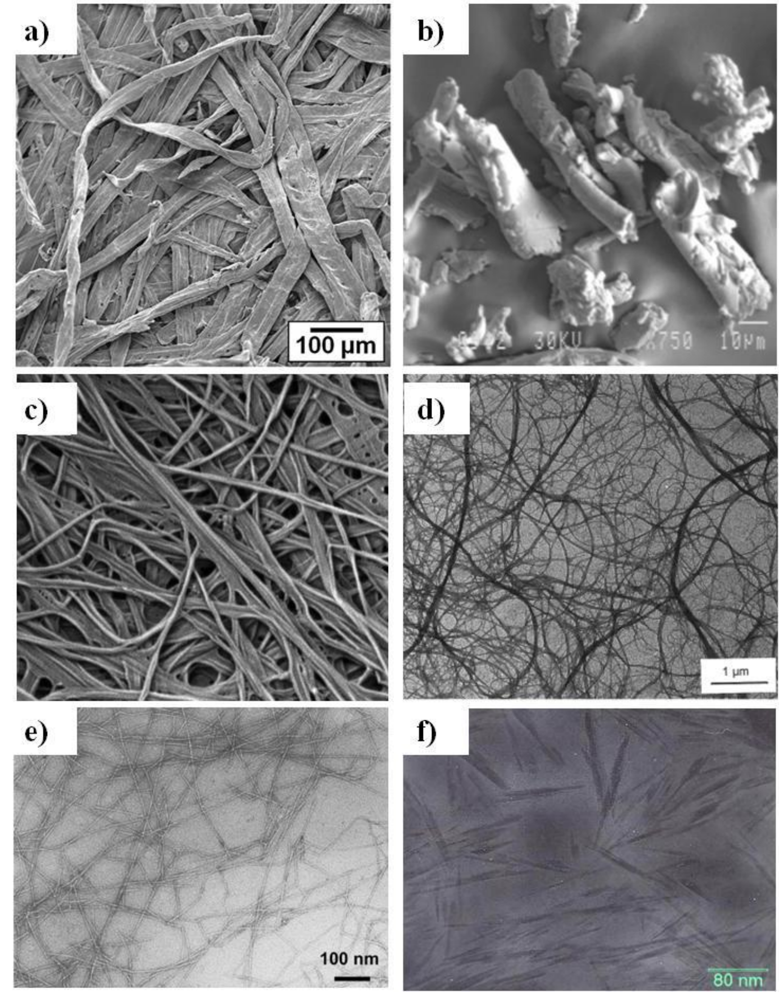
Microcrystalline cellulose

Bacterial cellulose

Microfibrillated cellulose

Nanofibrillated cellulose

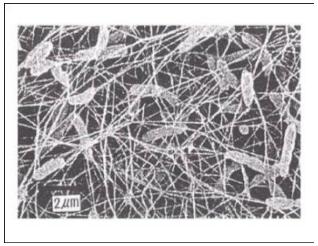
Cellulose nanocrystals



Moon *et al*., (2011)

Cellulose materials

e.g: Cellulose nanocrystals

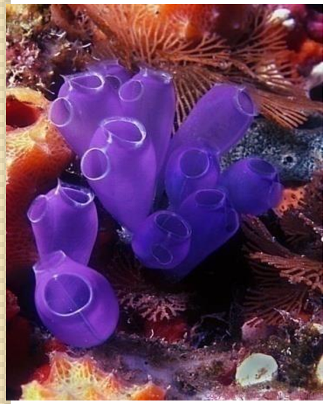


Bacterial

Sisal

Cotton

Source materials



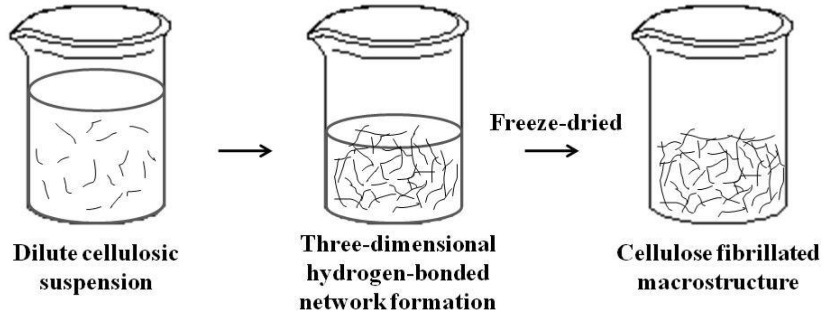
Tunicate

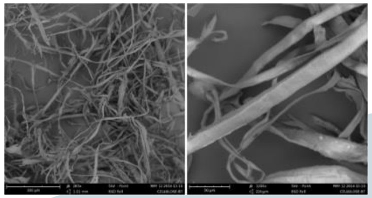
wastepaper

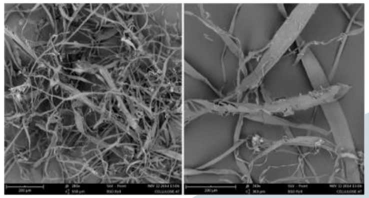
Ramie

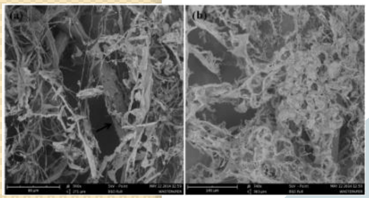
Mengkuang Leaves

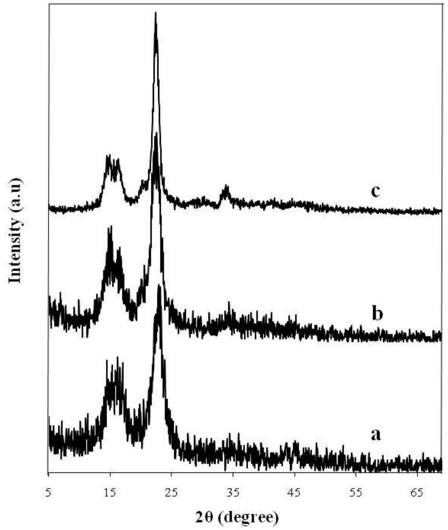
Nanomaterial











Controlled-condition of acid hydrolysis

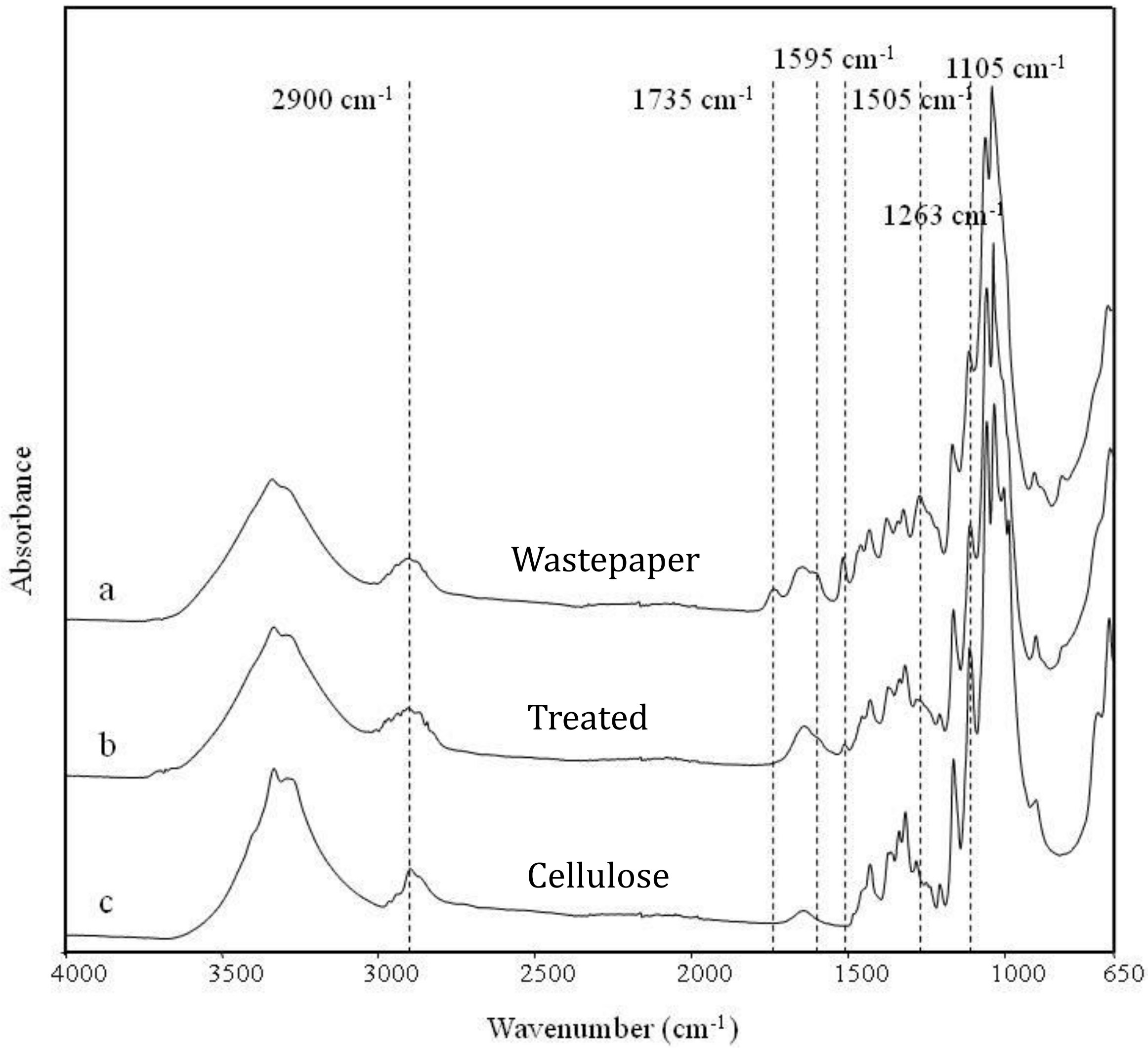
Alkali & Bleaching treatments

Pre-treatment of source material

Wastepaper

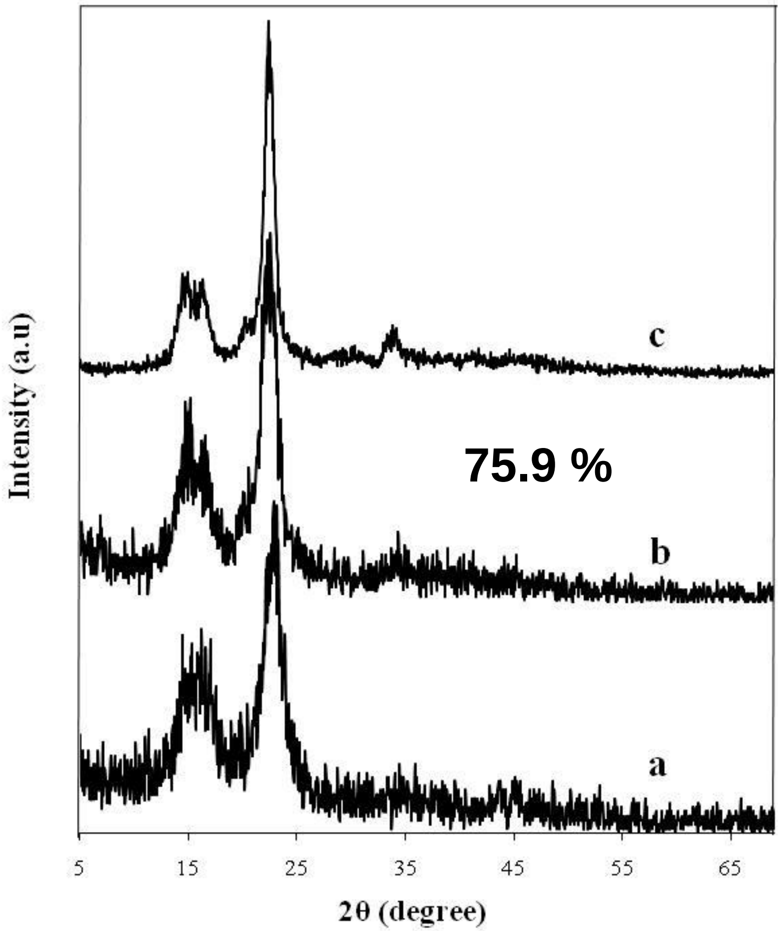
W. H. Danial et. al, Carbohydrate Polymers, 118, 165 (2015)

ATR-FTIR



W. H. Danial *et. a*l, *Carbohydrate Polymers*, 118, 165 (2015)

XRD Analysis



Segal's method (Segal *et al*., 1959)

$CrI = (I_{22.7} - I_{18}/I_{22.7}) \times 100\%$

CNCs (Pineapple leaf): 73.6 % Cherian et al., (2010)

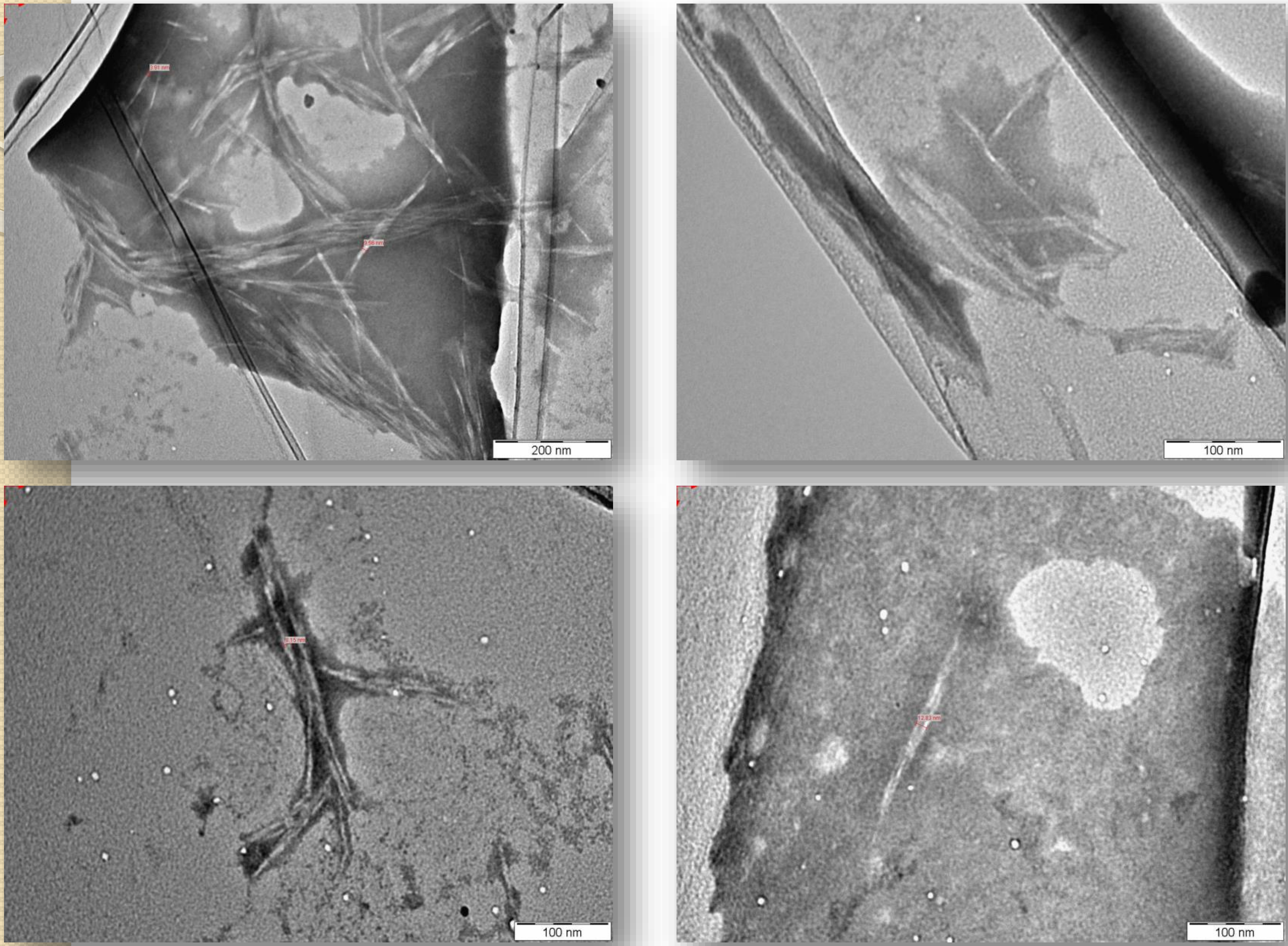
CNCs (mengkuang leaves): 65.9 % (Sheltami et al., (2012)

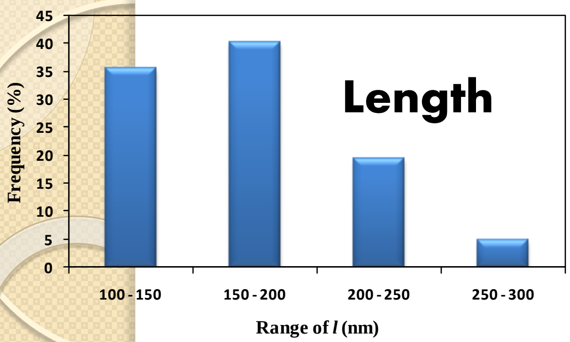
CNCs (Avicel): 81.0 % (Filson & Andoh et al., (2012)

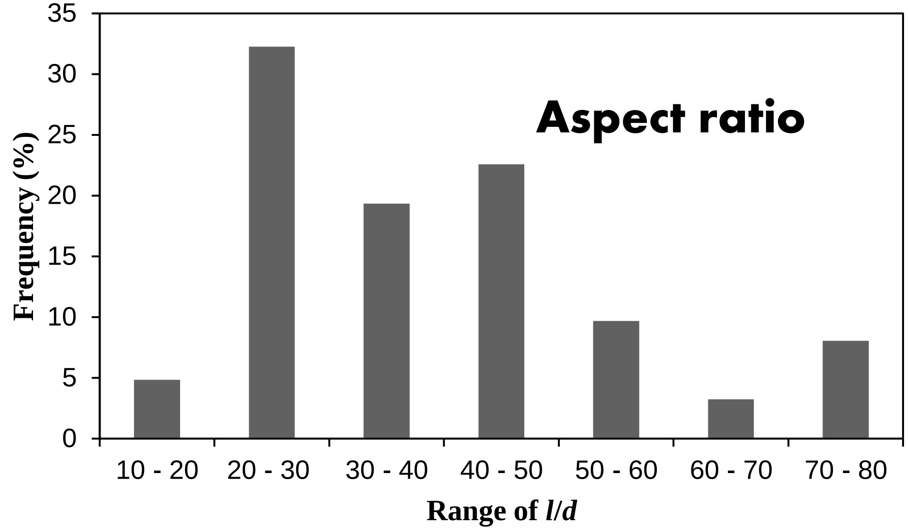
W. H. Danial *et. al*., *Carbohydrate Polymers*, 118, 165 (2015)

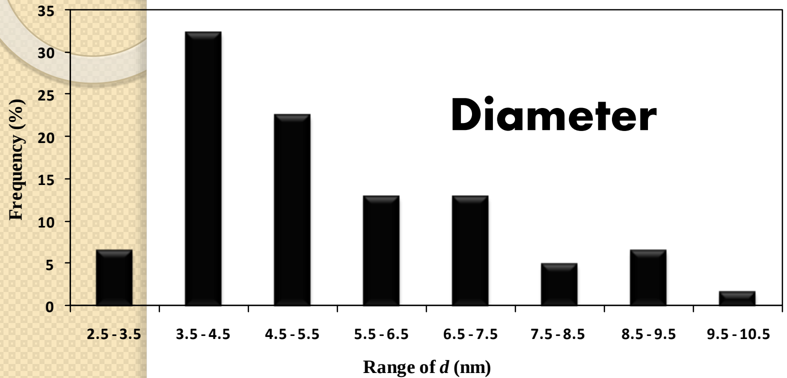
Isolation of CNCs

TEM Images









	Source Material	Length (nm)	Diameter (nm)
Uddin *et al.* (2011)	Cotton	100 – 150	10 – 15
Angles and Dufresne, (2008)	Tunicate	500 – 1000	10
Roman & Winter (2004)	Bacterial	100 – 1000	5 - 10
Peresin *et al.* (2010)	Ramie	100 – 250	3 – 10
Rodriguez *et al.* (2006)	Sisal	100 – 500	3 – 5
Sheltami *et al.* (2012)	Mengkuang Leaves	200	10 – 20
Beck-Candanedo et al., (2005)	Wood pulps	100 – 150	4 – 5
Danial *et al*. (2015)	Wastepaper	100 – 300	3 – 10

Key factor for composite preparation

❖ **Stable and homogenous graphene dispersion in a solvent (graphene solubilization)** → *insurmountable challenge in graphene composite processing*

"It is impossible to directly disperse hydrophobic graphite or graphene sheets in water without the assistance of surfactant or dispersing agents"

In order to achieve the solubility of graphene, the alteration of the graphene backbone is required through chemical modification (Park *et al.*, 2008, 2009), covalent (Stankovich *et al.*, 2006c; Strom *et al.*, 2010) or non-covalent (Stankovich *et al.*, 2006b; Qi *et al.*, 2010) functionalization

To achieve graphene dispersibility

Surfactant assisted electrochemical exfoliation (extremely stable suspension)

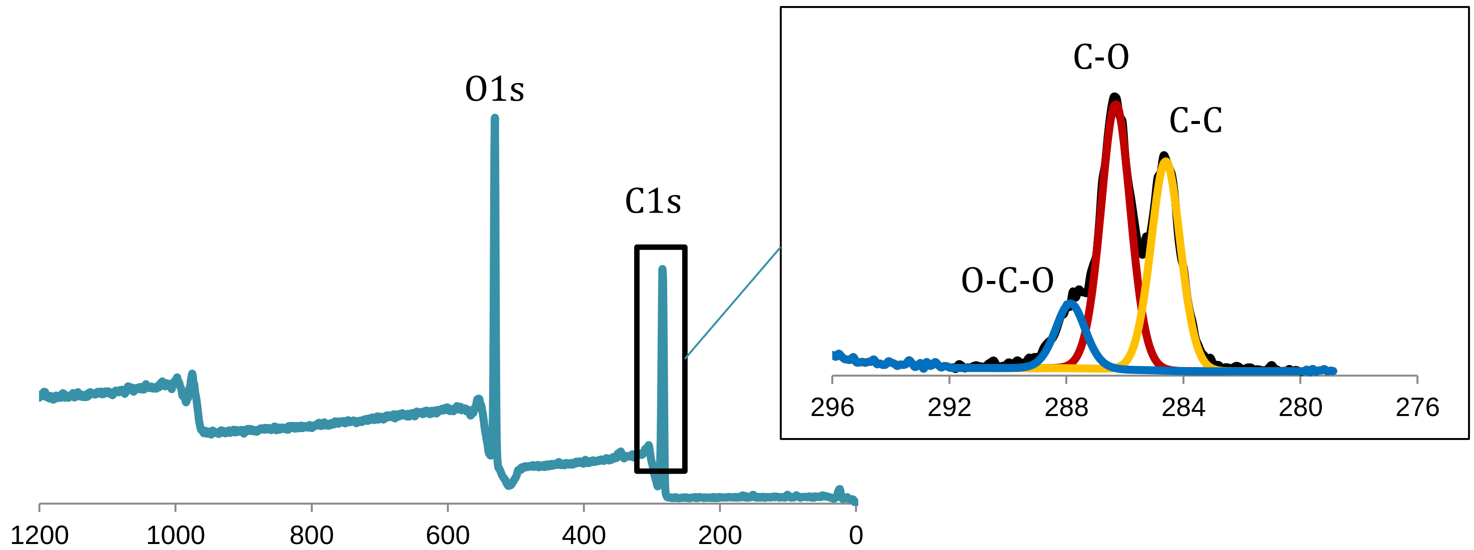
Ultrasonication (short –time metastable suspension)

Graphene oxide

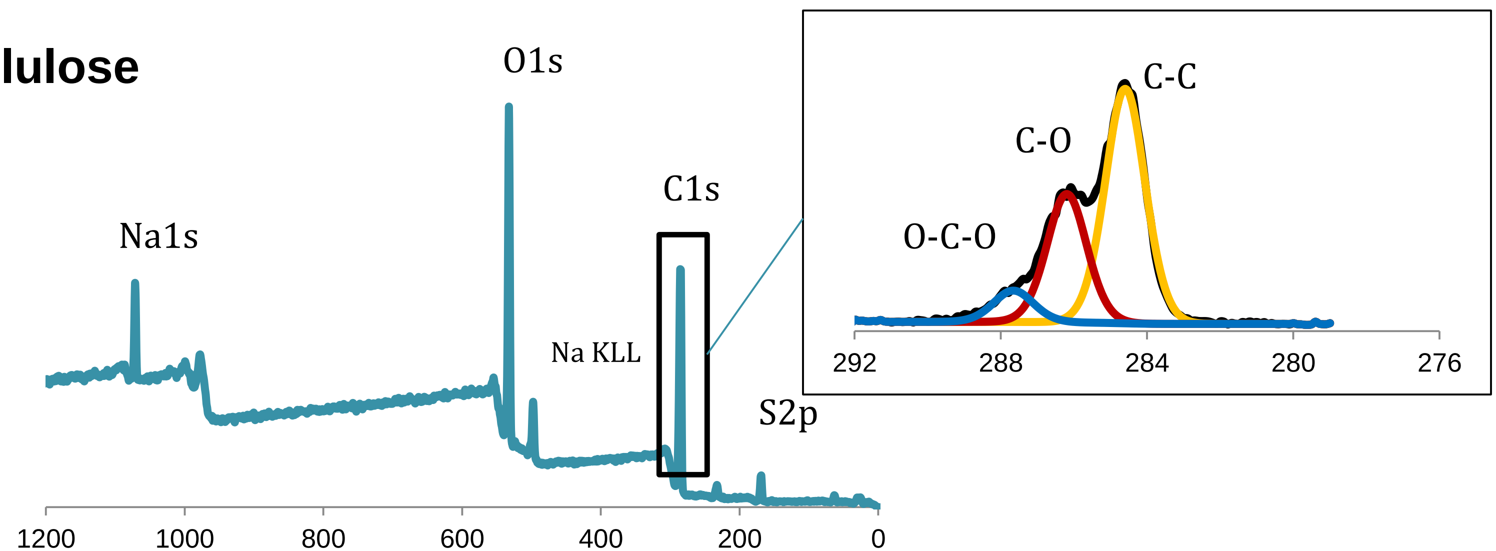
Reduced graphene oxide

XPS Analysis

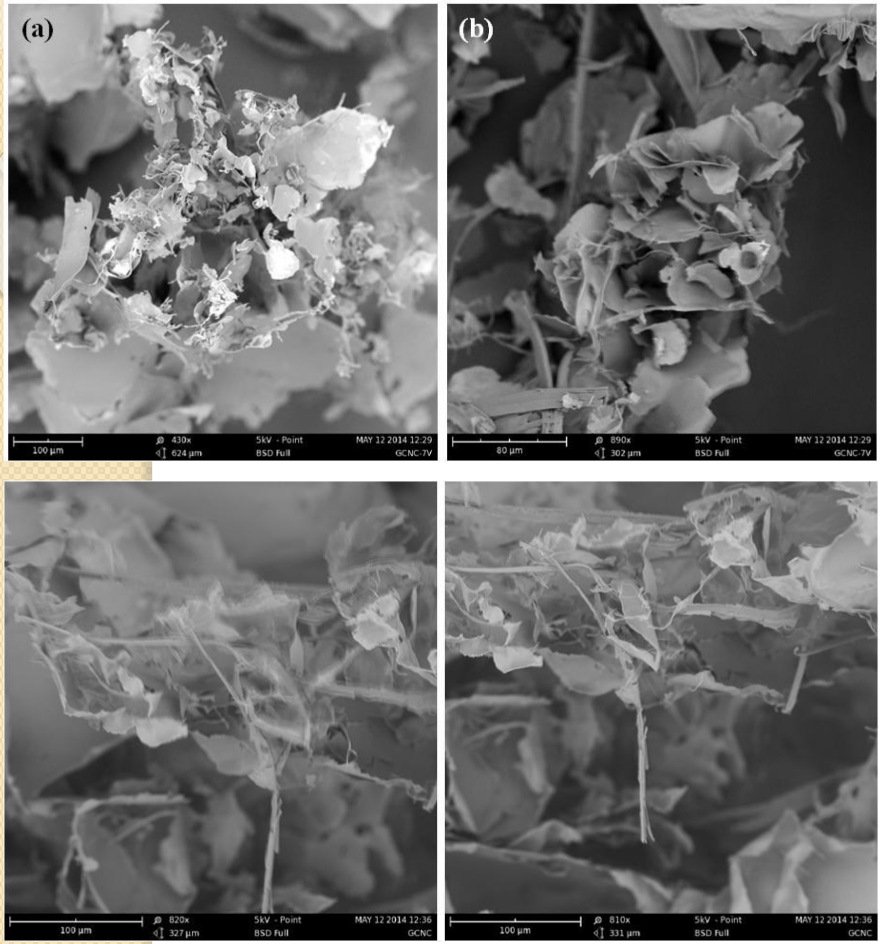
Cellulose

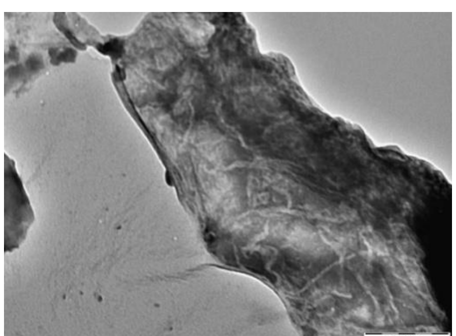


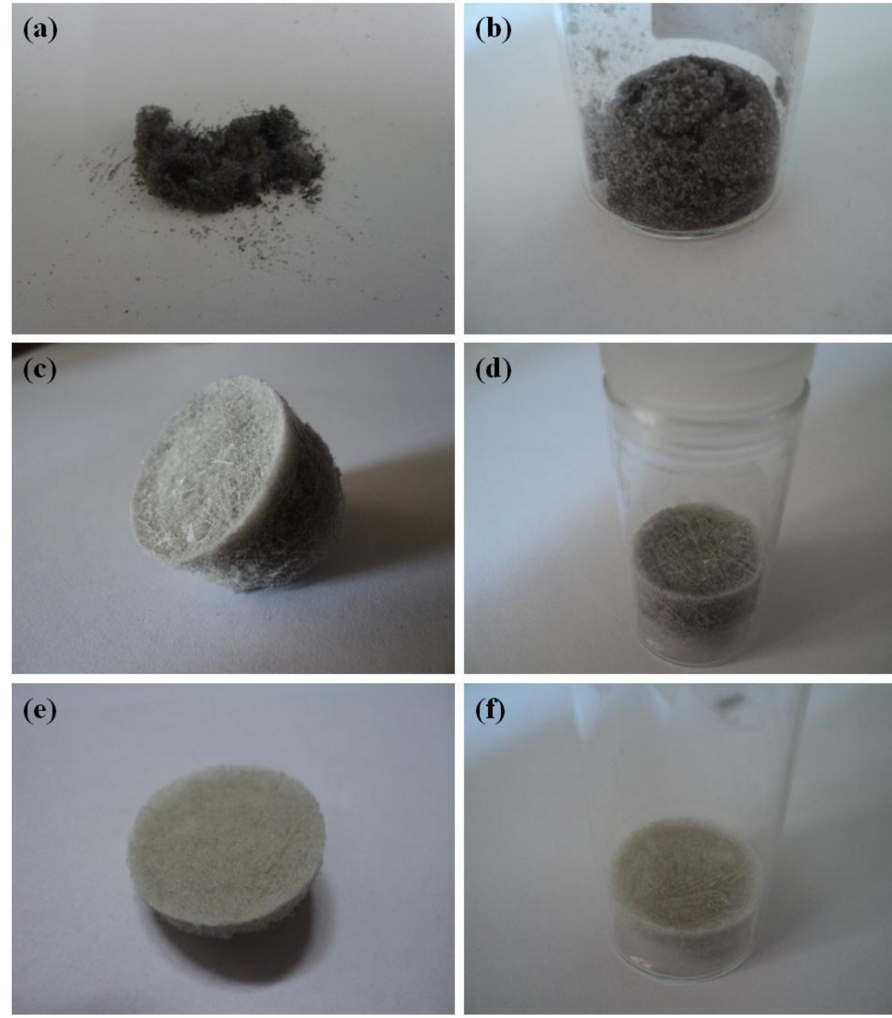
Graphene-Cellulose



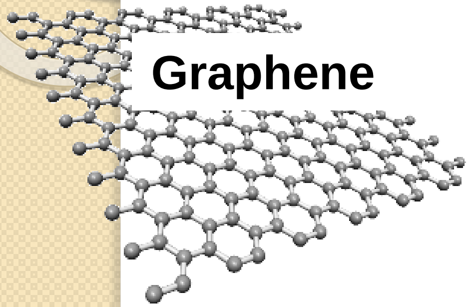
Graphene-Cellulose fibrillated structure





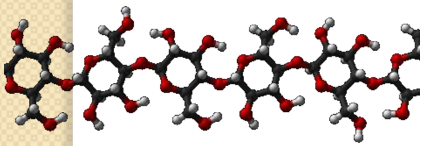


The marriage chemistry of graphene & cellulose



Graphene → **Hydrophobic**

Cellulose → **Amphiphilic**

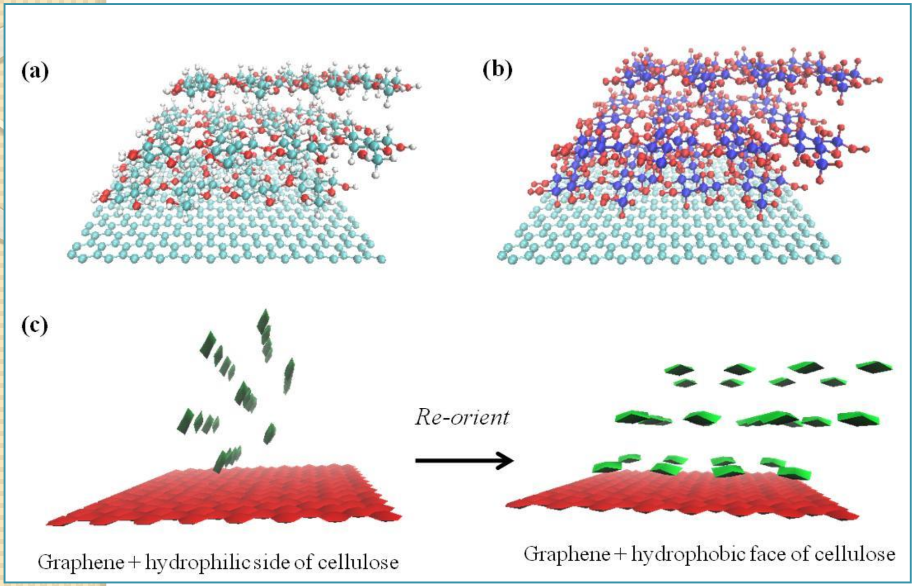


Hydrophobic interactions

"***Lindman effect***"

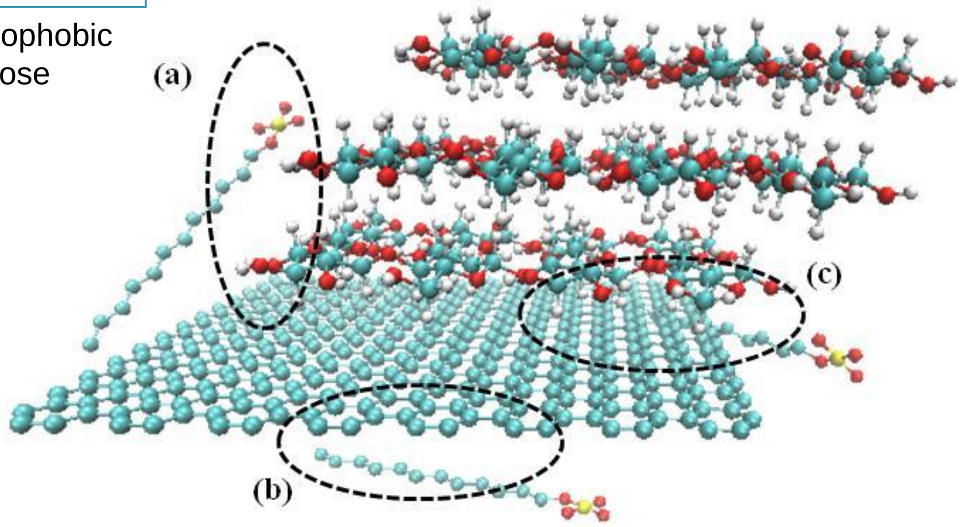
Lindman *et al*, *J Molecular Liquids*, 156, 76 (2010)

Visual molecular dynamics



Graphene + hydrophilic side of cellulose

Graphene + hydrophobic side of cellulose



❖The electrochemical preparation of graphene using two-electrode cell system can be achieved

❖ The reuse of wastepaper for the extraction of cellulose material

❖ Green approach of the production of nano-material from the waste substance

❖ Can be scaled-up, high availability and low-cost precursor

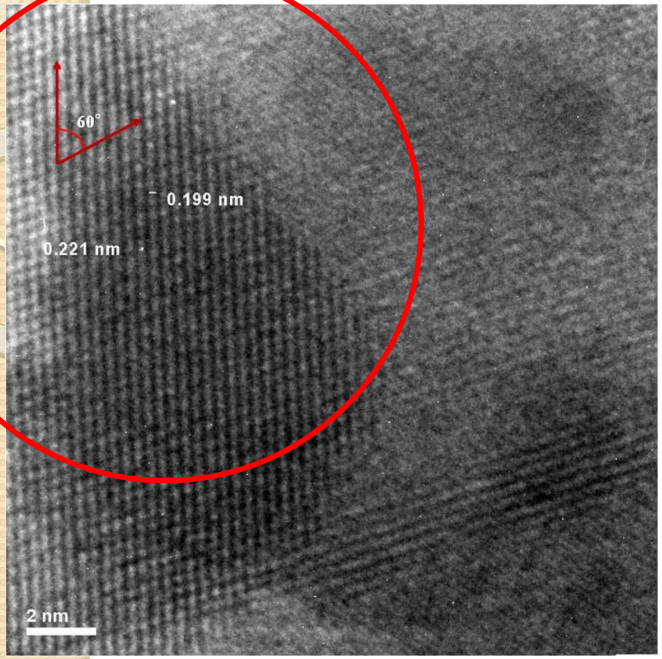
❖Graphene and cellulose material both known to be interesting reinforcing material with exceptional reinforce capability for composite (e.g: polymer) preparation.

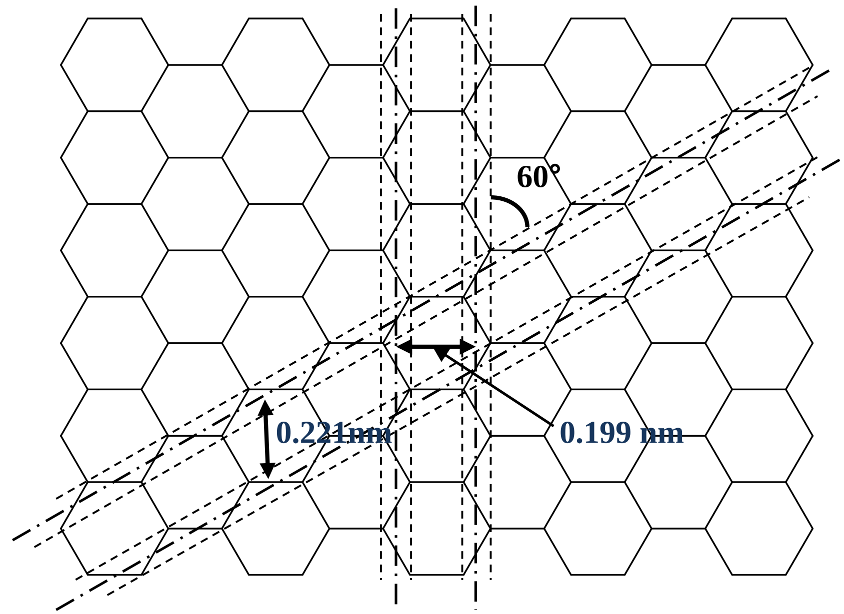
Reinforcing ability

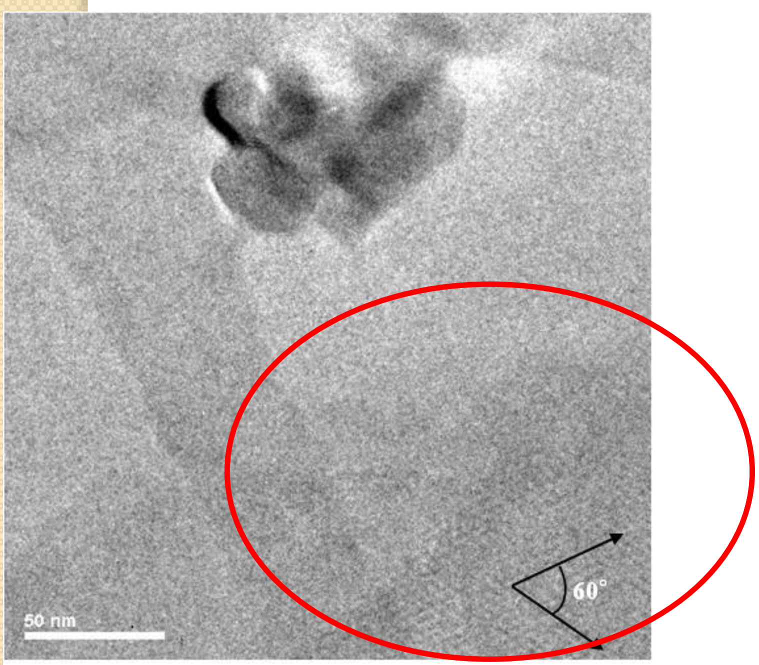
- Graphene ✓
- Cellulose nanomaterial ✓
- Graphene-cellulose ✓

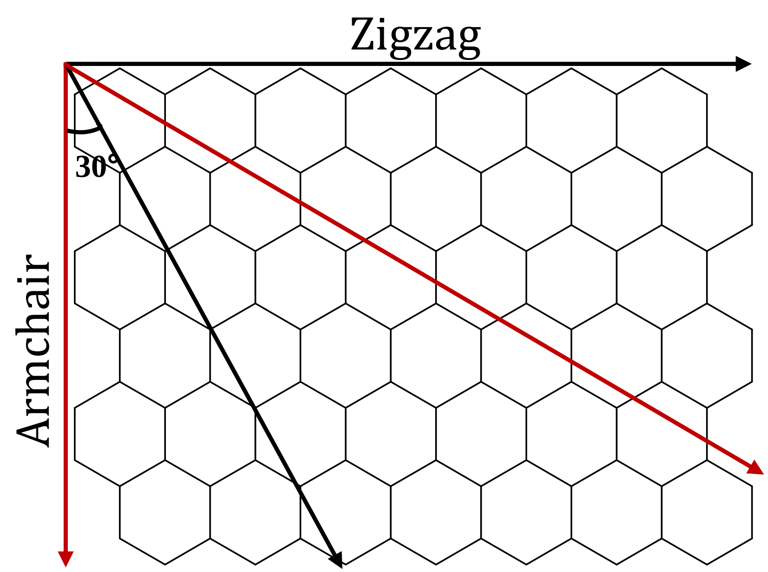
Polymer film

HRTEM Images

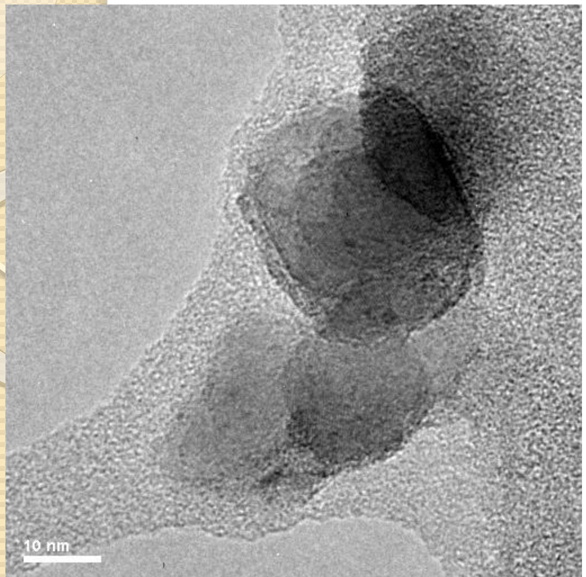




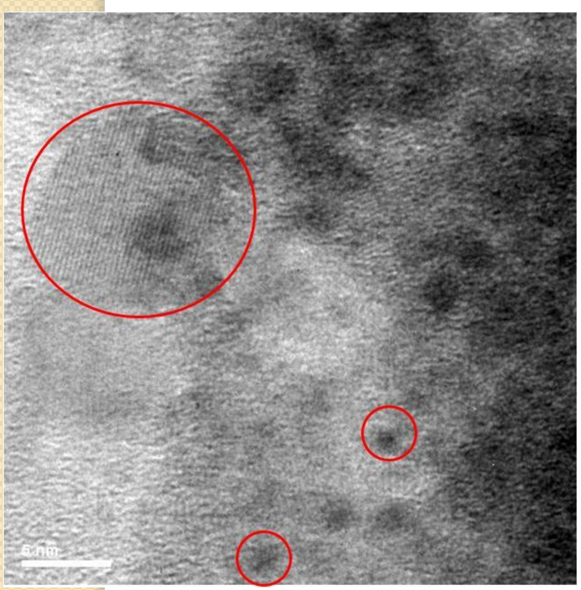


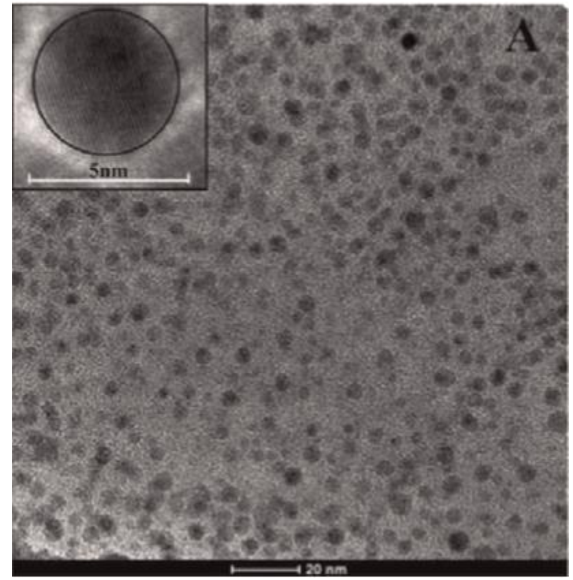


Graphene Quantum Dots (GQDs)



Small width surface of **relatively transparent** graphene layer





He et al., *Biosensors and Bioelectronics*, 74, 418 (2015)

Raman Analysis

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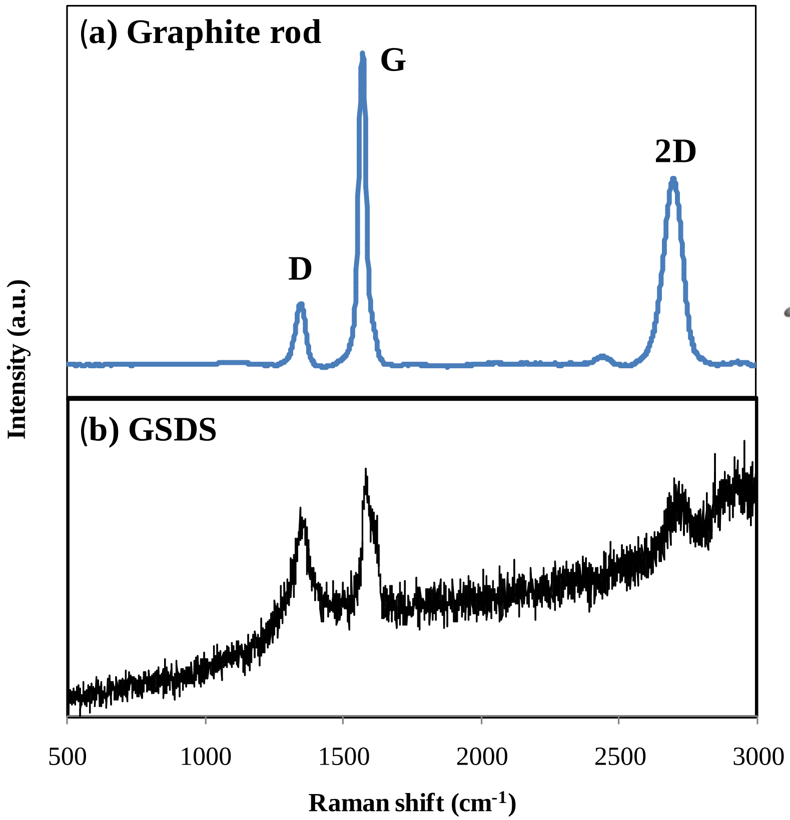
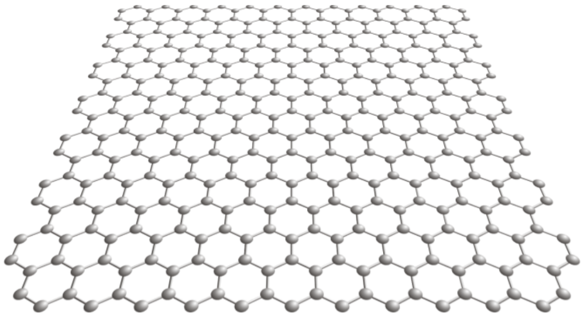
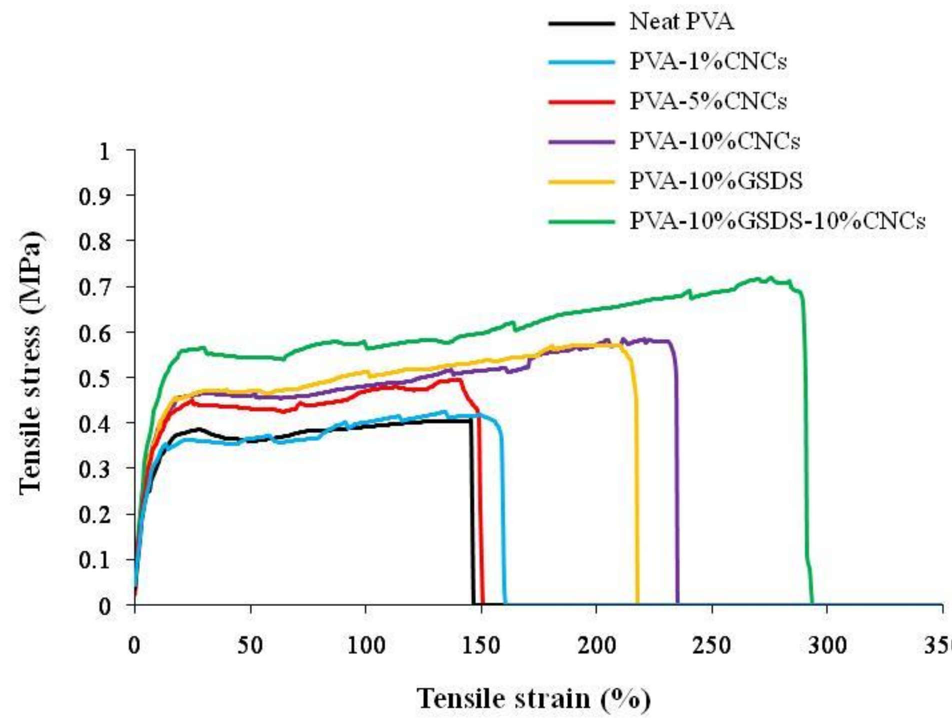


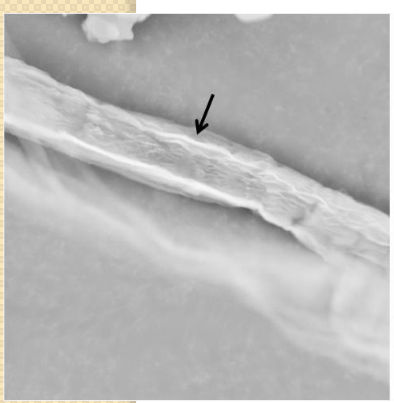


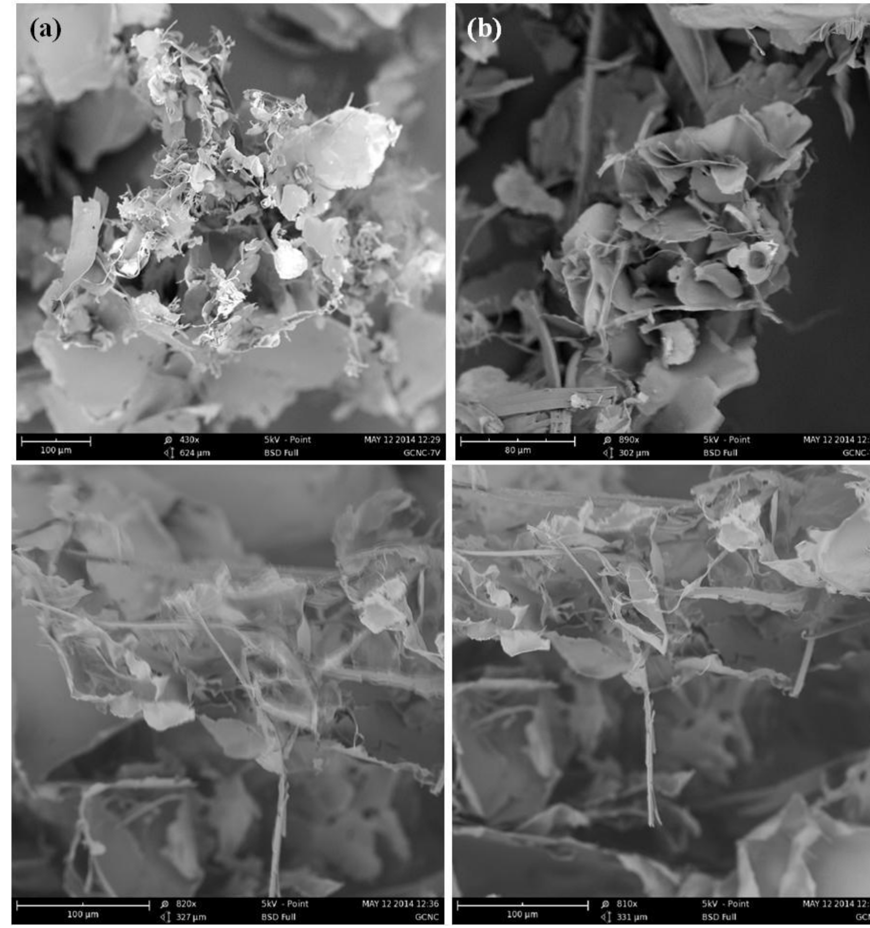
Reinforcing capability in polymer composite application

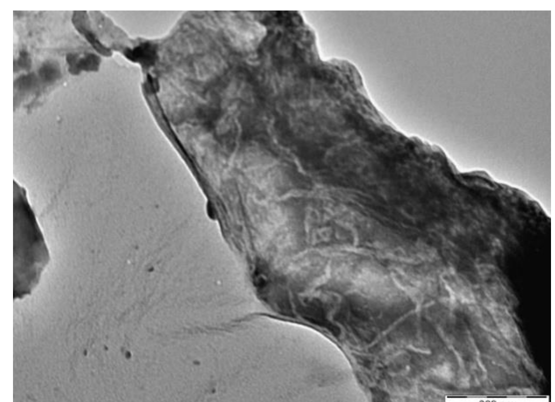


Reinforcing ability → Graphene ✓ / CNCs ✓ / Graphene-CNCs ✓

Graphene-CNCs Aerogel







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Thank You for your attention!