

# Physicochemical Evaluation of Carbon-based Nanomaterial Exposure from Carbon Fiber Processing Laboratory

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Industrial Centre of Innovation in Biomedical  
SIRIM Industrial Research  
SIRIM Berhad, Kulim Hi-Tech Park



- 01 Introduction and Motivation

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- 02 Scope : material, location, experimented subject

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- 03 Sampling – air sampling & dermal simulation

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- 04 Physicochemical assessment – microscopy & chemical

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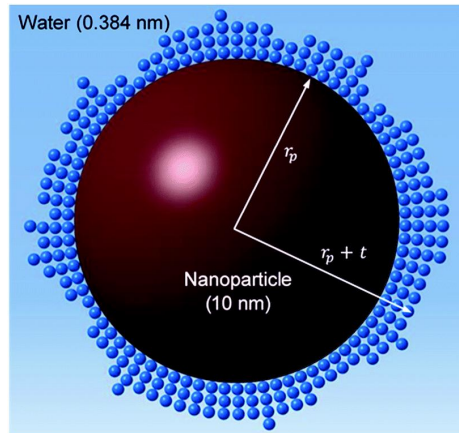
- 05 Risk assessment & Control Measures

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- 06 Conclusion

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# Introduction & Motivation

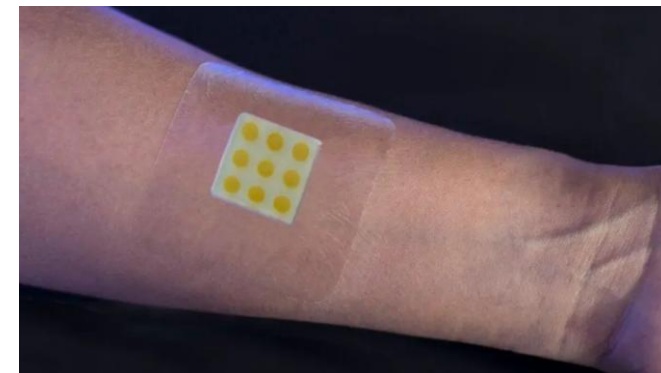


## European Commission

Particle size of at least half of the particle in the number size distribution - 100 nm or below

Can occur

- Naturally
- Be created purposely
- As by product

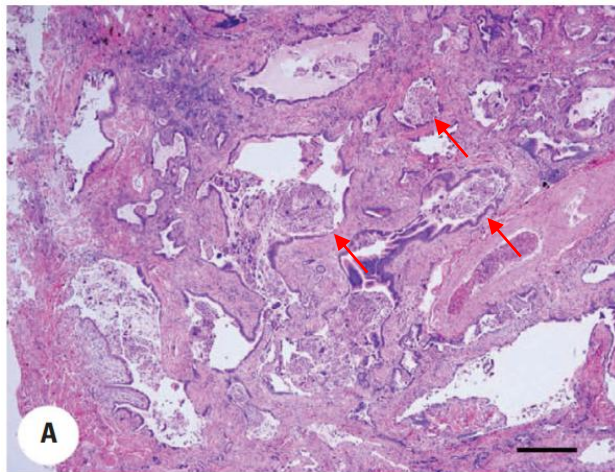


However the same properties that make  
nanomaterials scientifically and commercially  
exploitable

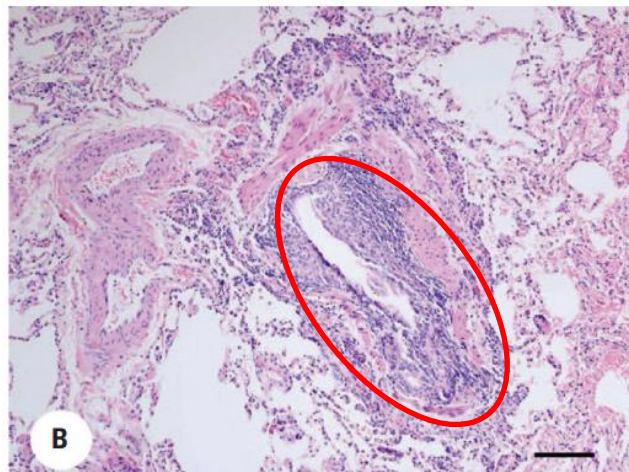
..are also the basis of possible health effects  
especially on by-product – risk of occupational

## Case Report: Lung Disease in World Trade Center Responders Exposed to Dust and Smoke: Carbon Nanotubes Found in the Lungs of World Trade Center Patients and Dust Samples

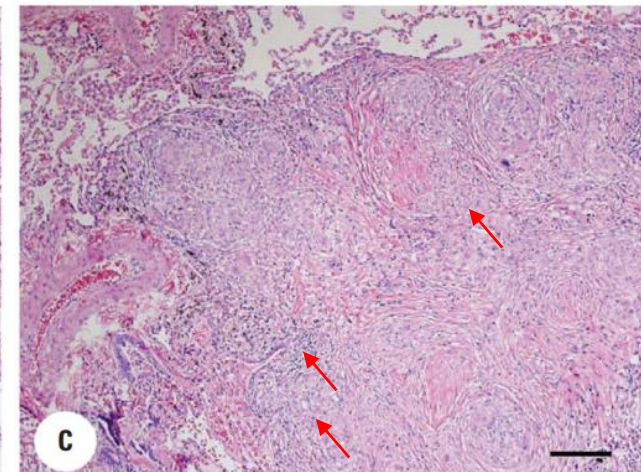
*Maoxin Wu,<sup>1</sup> Ronald E. Gordon,<sup>1</sup> Robin Herbert,<sup>2</sup> Maria Padilla,<sup>3</sup> Jacqueline Moline,<sup>2</sup> David Mendelson,<sup>4</sup> Virginia Litle,<sup>5\*</sup> William D. Travis,<sup>6</sup> and Joan Gil<sup>1</sup>*



**A** Honeycomb fibrosis with cyst remodeling of lung parenchyma

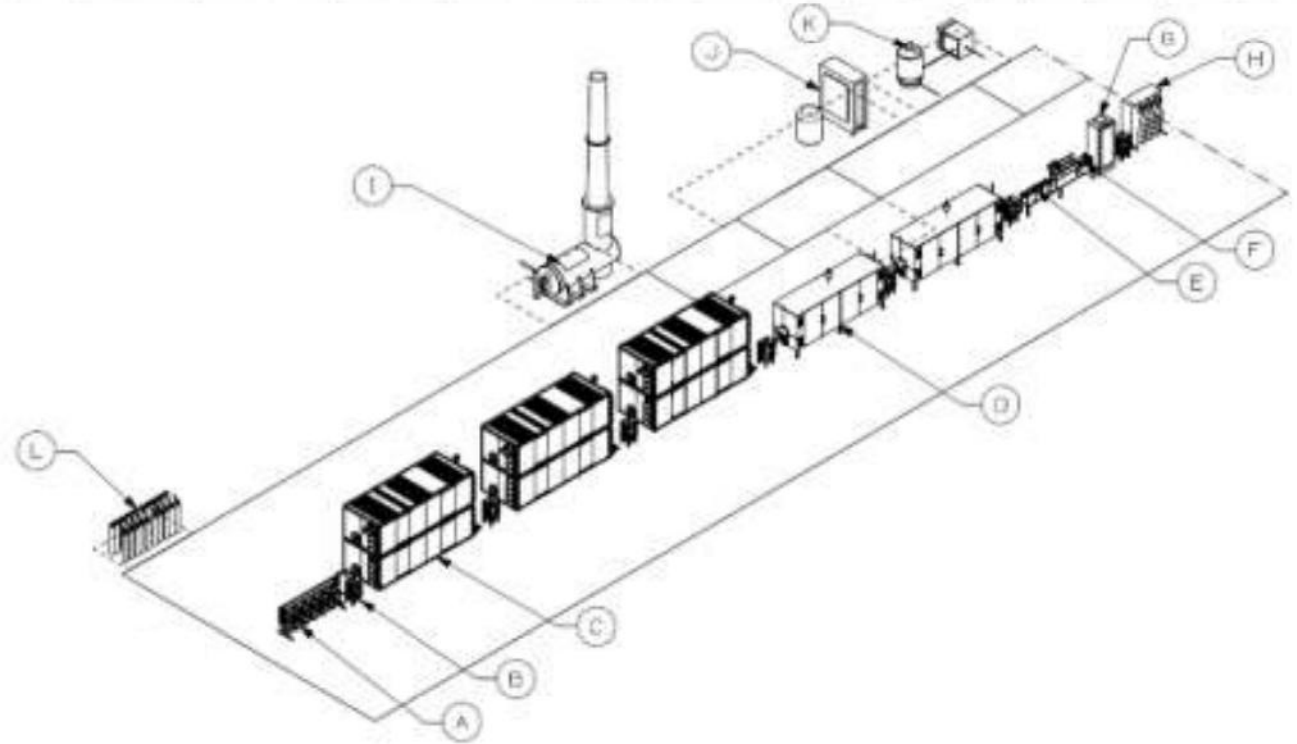


**B** Chronic bronchiolitis : inflammation in submucosa of respiratory epithelium



**C** Granuloma in interstitium

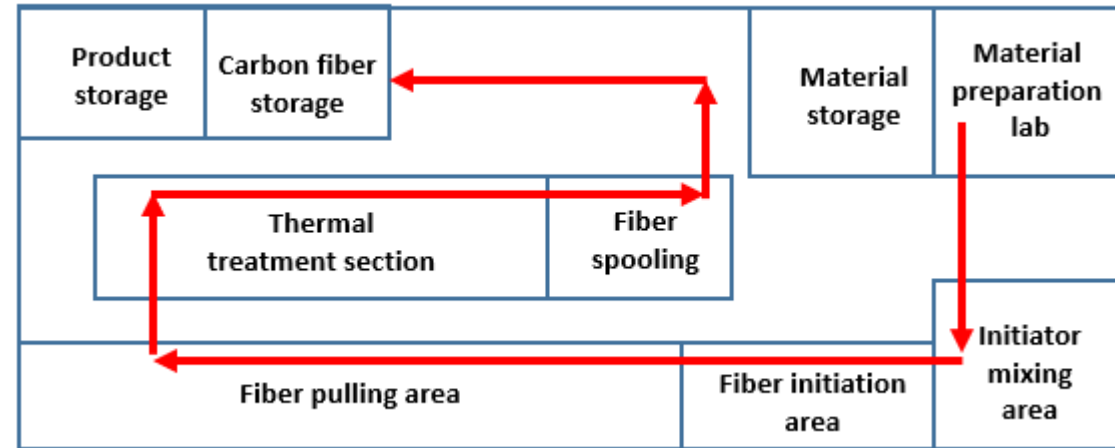
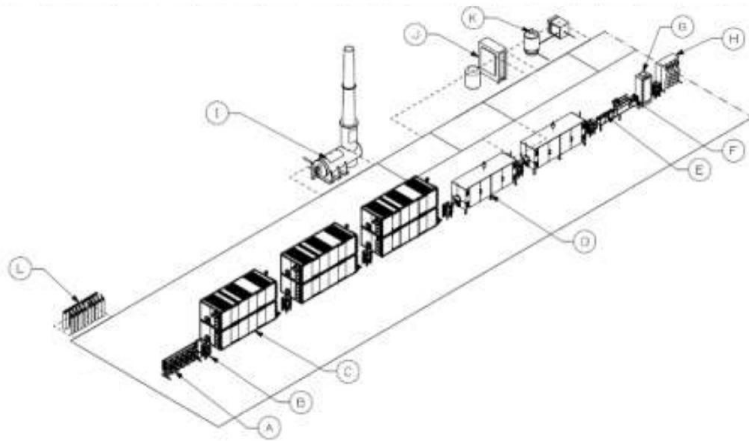
# Testing Location



**Carbon Fiber Laboratory  
Advanced Materials Research Centre  
SIRIM Berhad  
Kulim HiTech Park Kedah**

**Schematic layout of Carbon Fiber Pilot Plant in SIRIM Kulim**

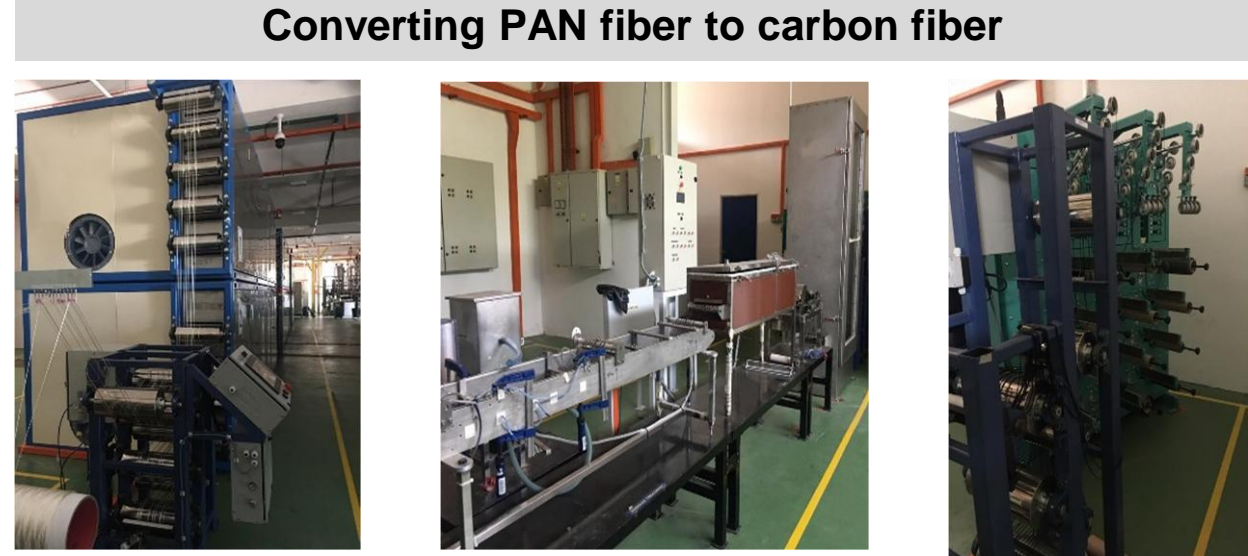
# Testing Location



**Spin dope preparation**



**Spinning**



**Stabilisation & Carbonisation Process**

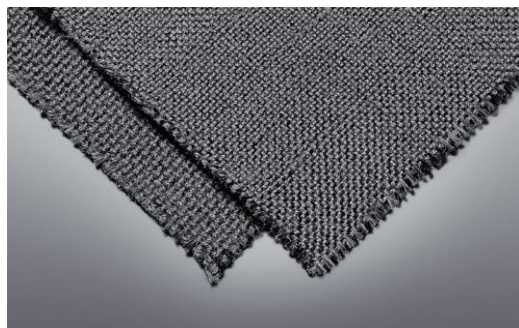
**Surface Treatment & Sizing**

**Spooling**

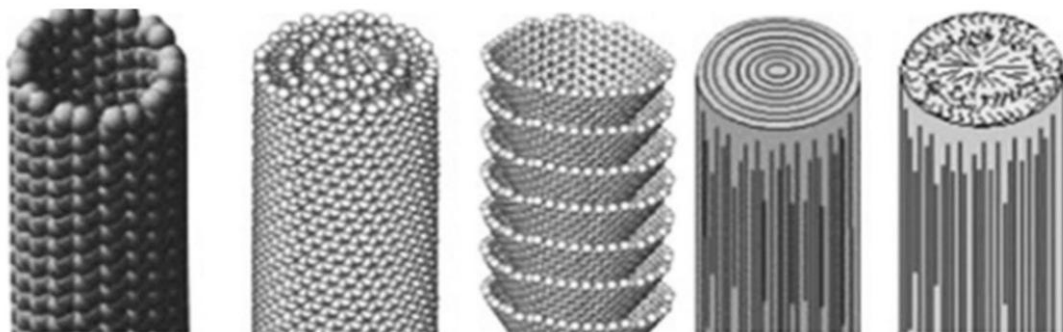
# Scopes of Nanomaterials



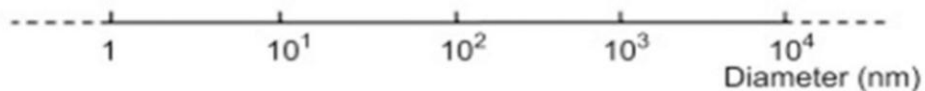
The product -  
Carbon Fiber yarn



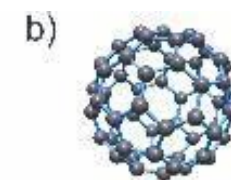
Carbon matt



Carbon nanotube      Carbon nanofiber      Carbon fiber



Carbon Dots



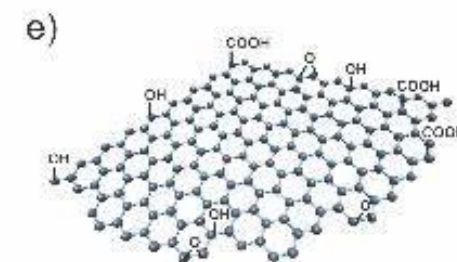
Fullerene



Carbon Nanotube



Graphene



Graphene Oxide

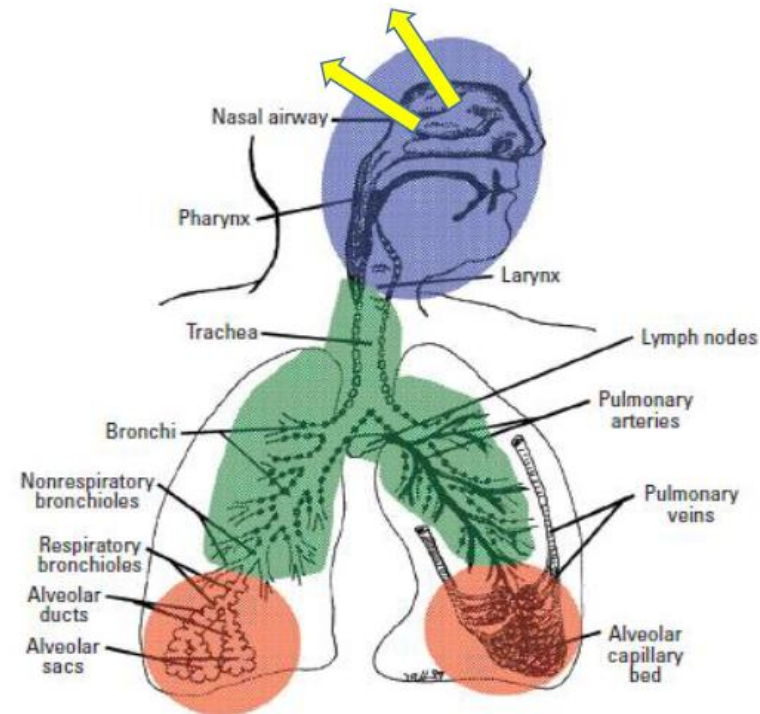
**Possible carbonaceous  
nanomaterial exposure**



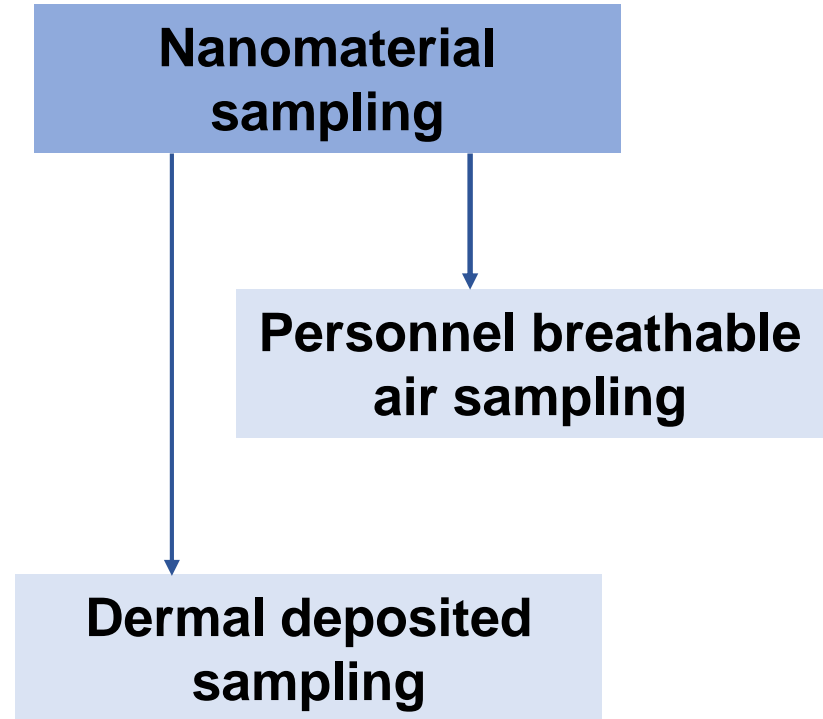
TECHNICAL REPORT  
**Occupational Exposure Sampling  
for Engineered Nanomaterials**



**NIOSH : CDC  
Sampling on  
nanomaterials**



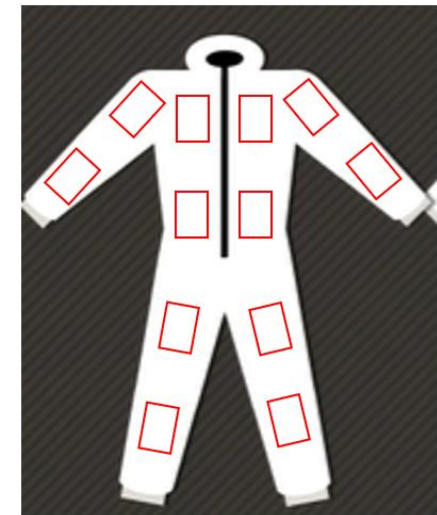
**Transport shall be  
through personnel  
breathable tract**



## Personnel breathable air sampling



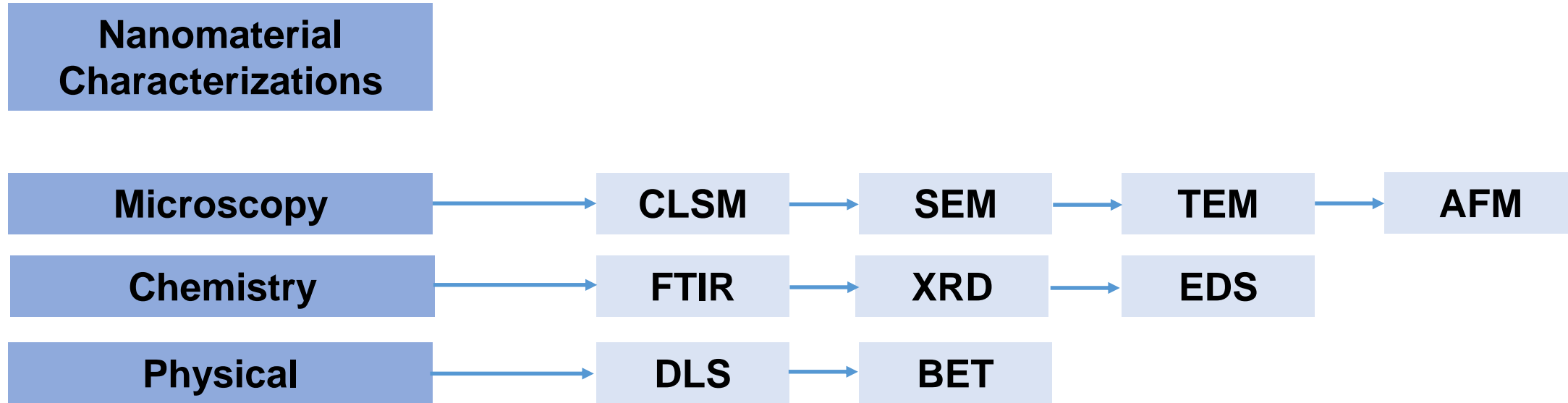
## Dermal deposited sampling



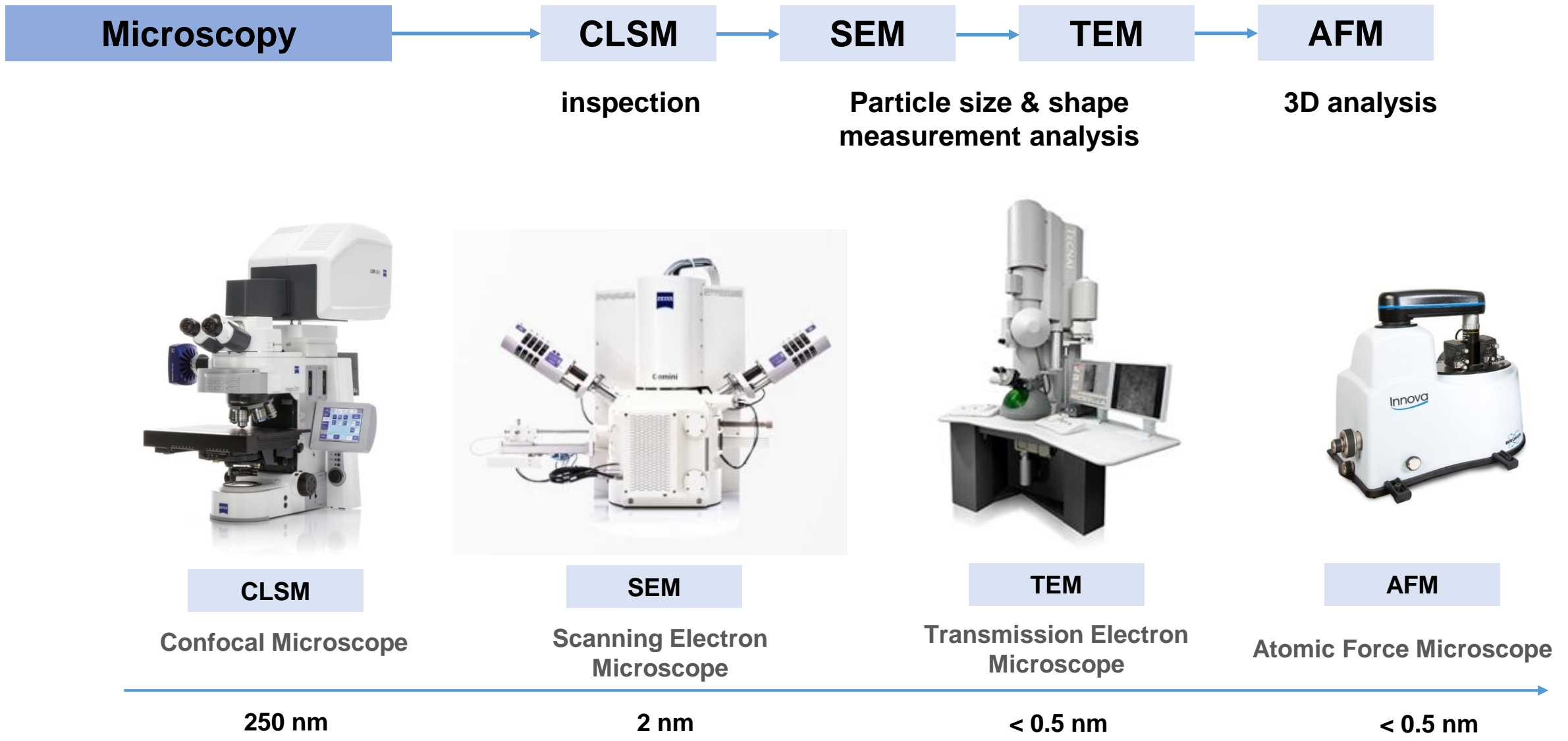
**Points of sample  
collection**

**SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>  
membrane plate**

# Physicochemical Characterizations

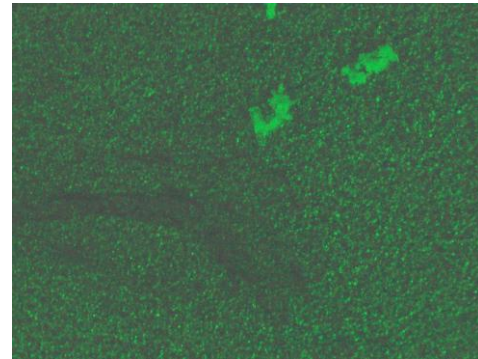


# Physicochemical Characterizations

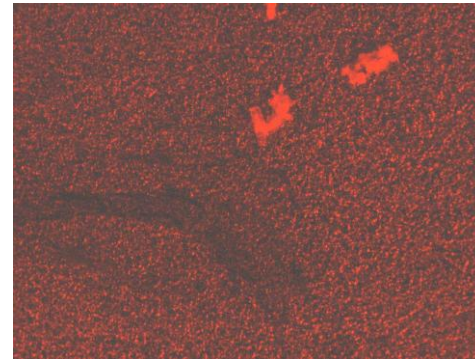




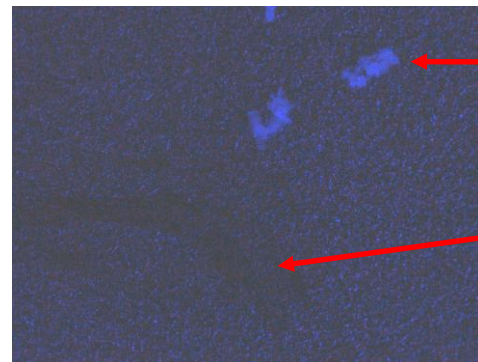
CLSM



Visible range illumination



NIR range illumination

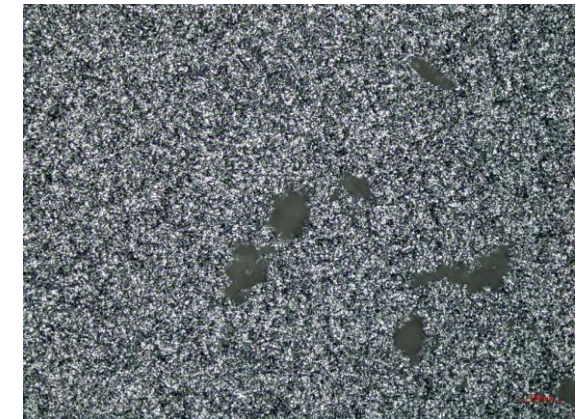


UV range illumination

Non- carbonaceous areas

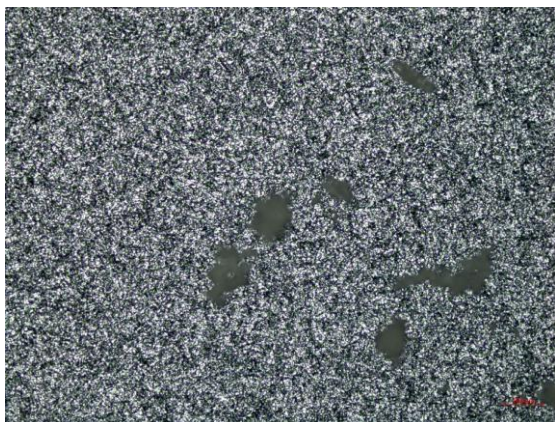
Carbonaceous areas

Inspection on possible areas of carbonaceous nanomaterial deposition

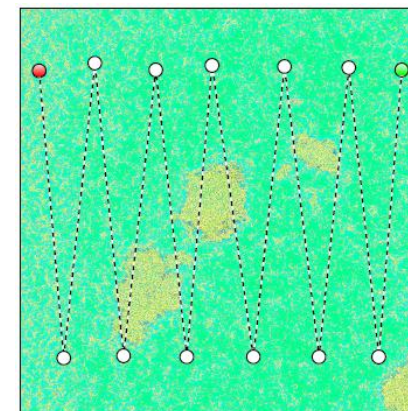
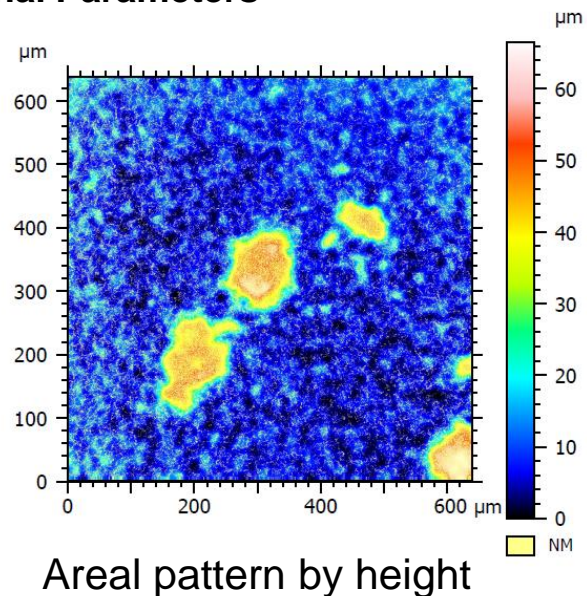


Magnification 400x

## Confocal Laser Scanning Microscopy – Functional Parameters

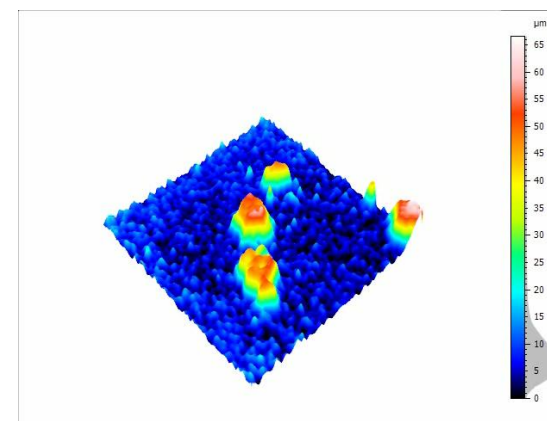
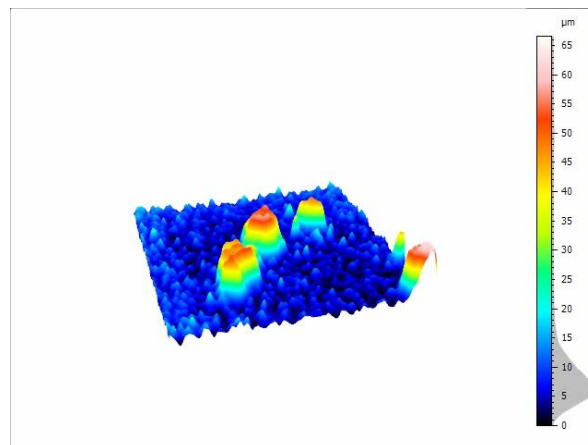


Magnification 400x



Line profile analysis

3D imaging by circle path-view

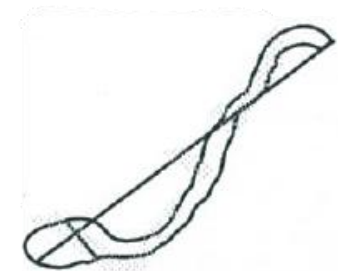
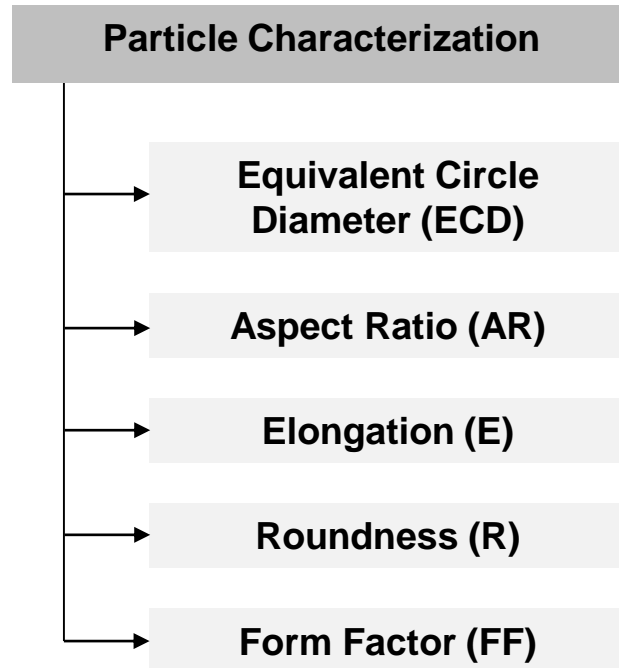




## Particle Characterizations by Microscopic Techniques

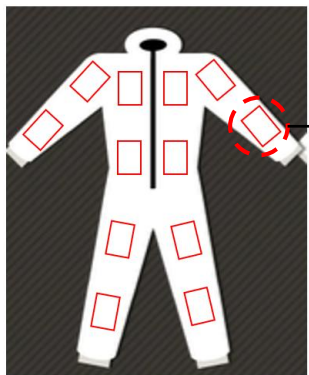


Standard Practice for  
Characterization of Particles

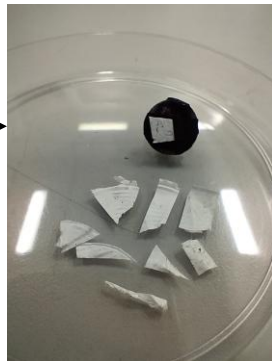


# Physicochemical : Microscopy

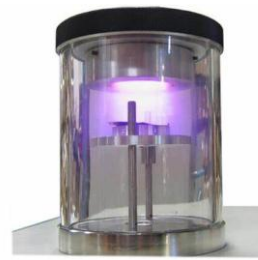
## Microscopic Analysis by SEM on Morphology and Uniformity



SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> membrane plate



Cut and place on SEM stub



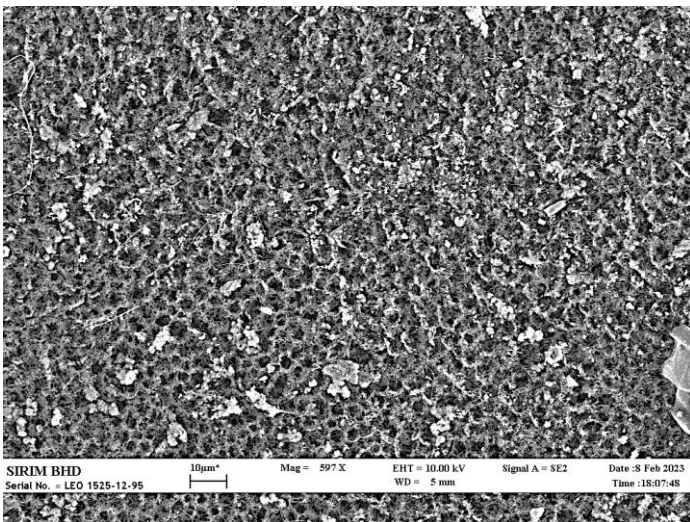
Sputtering

Platinum/Gold coated  
Vacuum  
t = 120 s

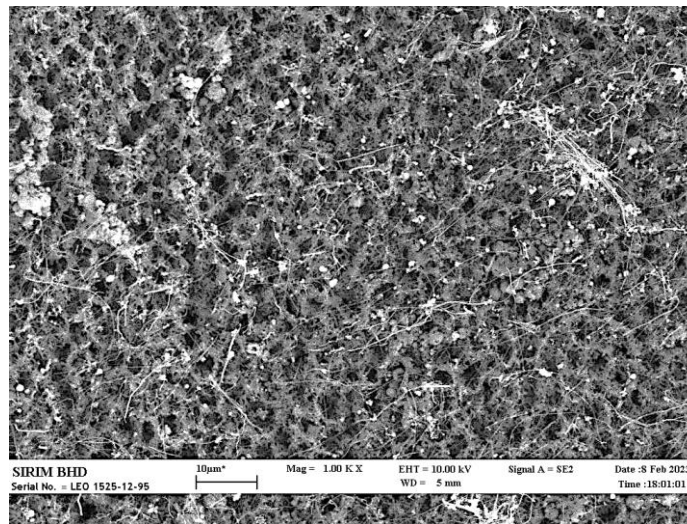


Imaging by FESEM

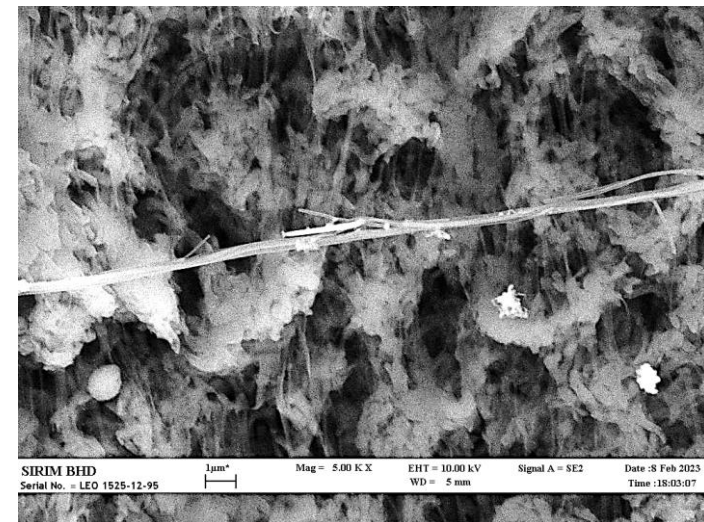
EHT : 10 KV  
Magnification : 1KX, 5 KX, 10 KX



500 x – arm position



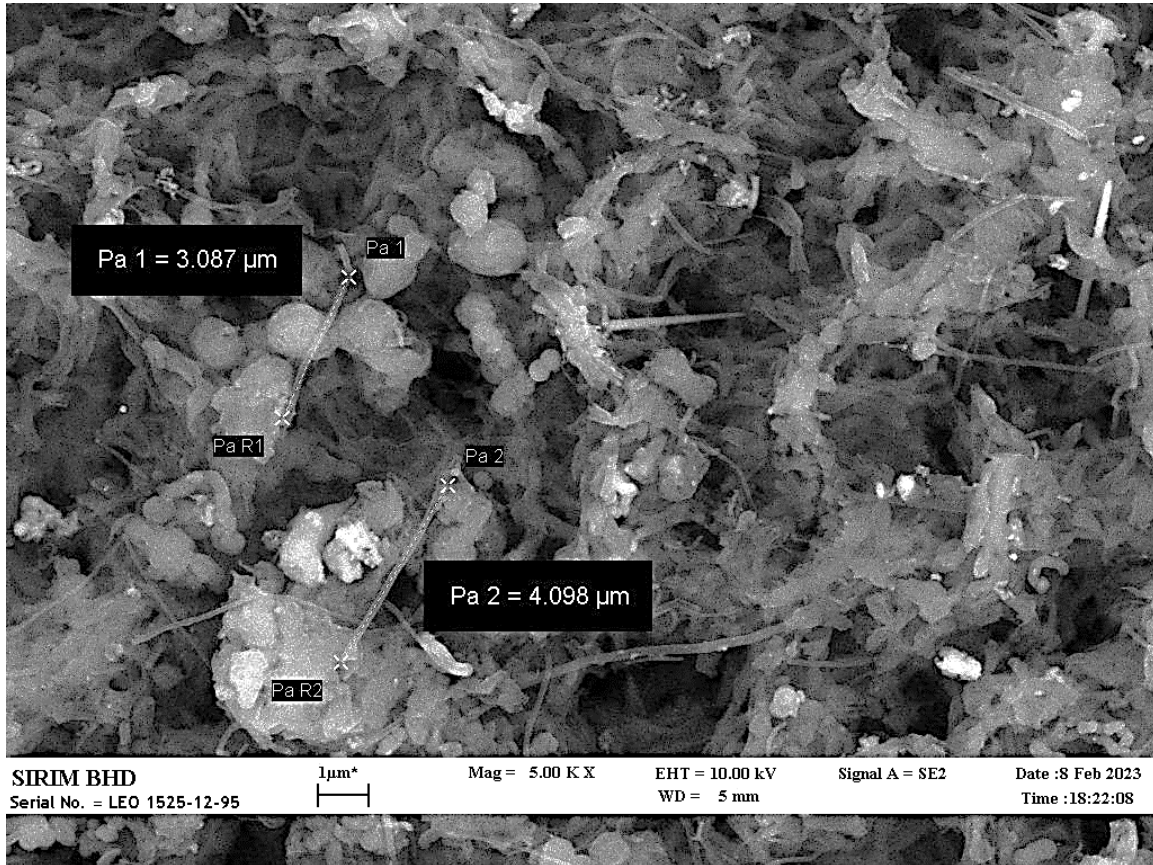
1000 x



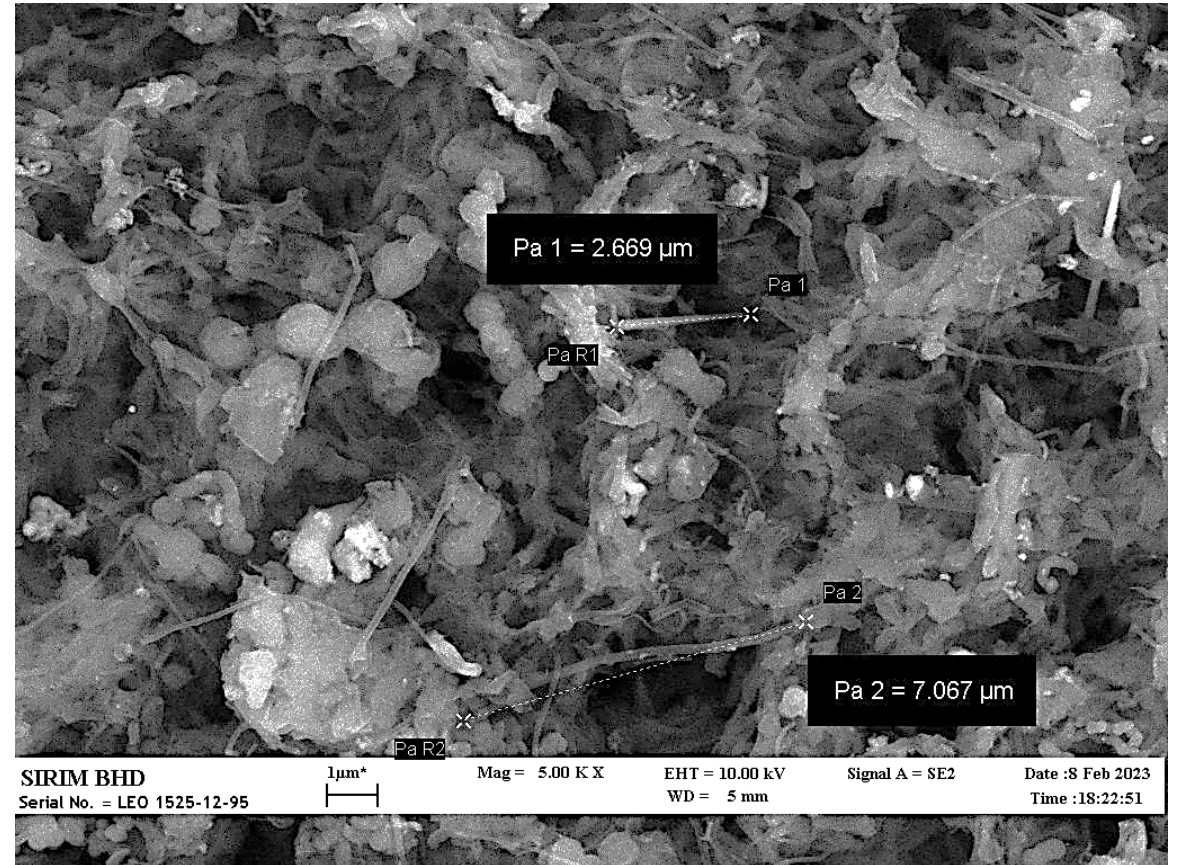
5000 x



## Microscopic Analysis by SEM – Size in Length



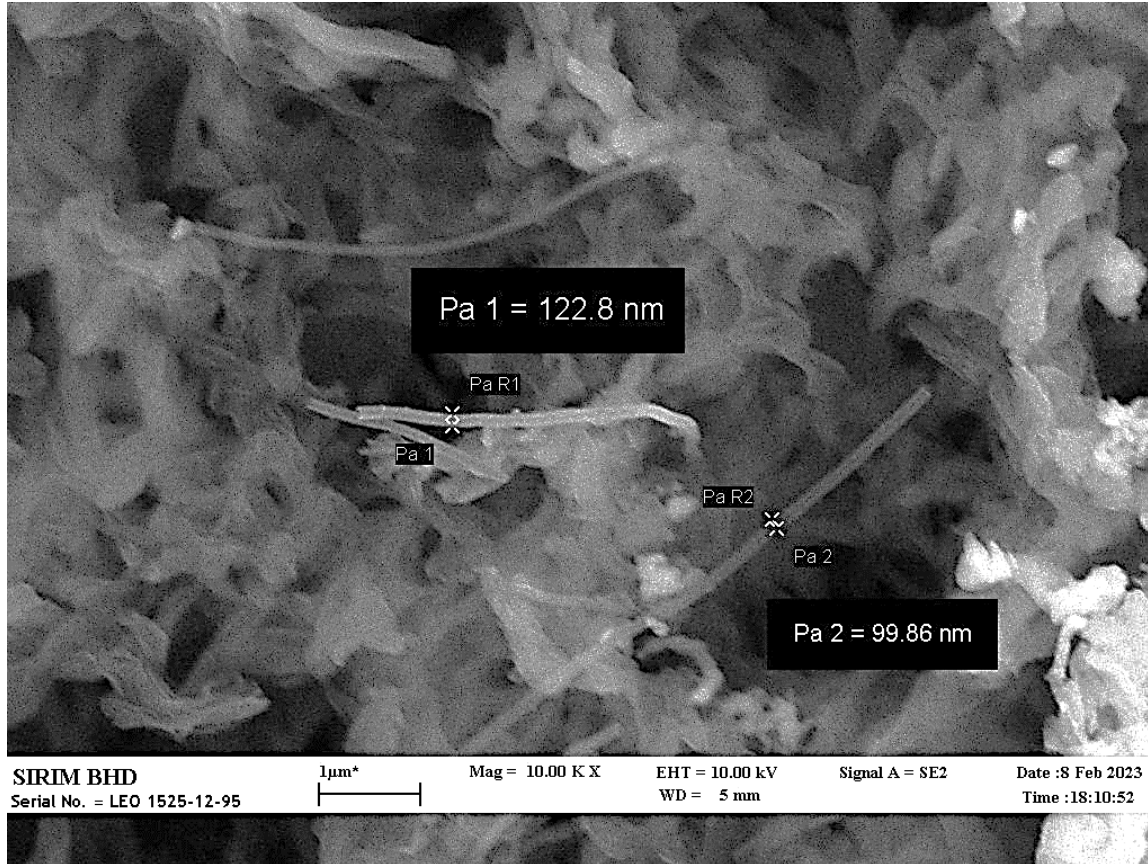
5000 x, chest position



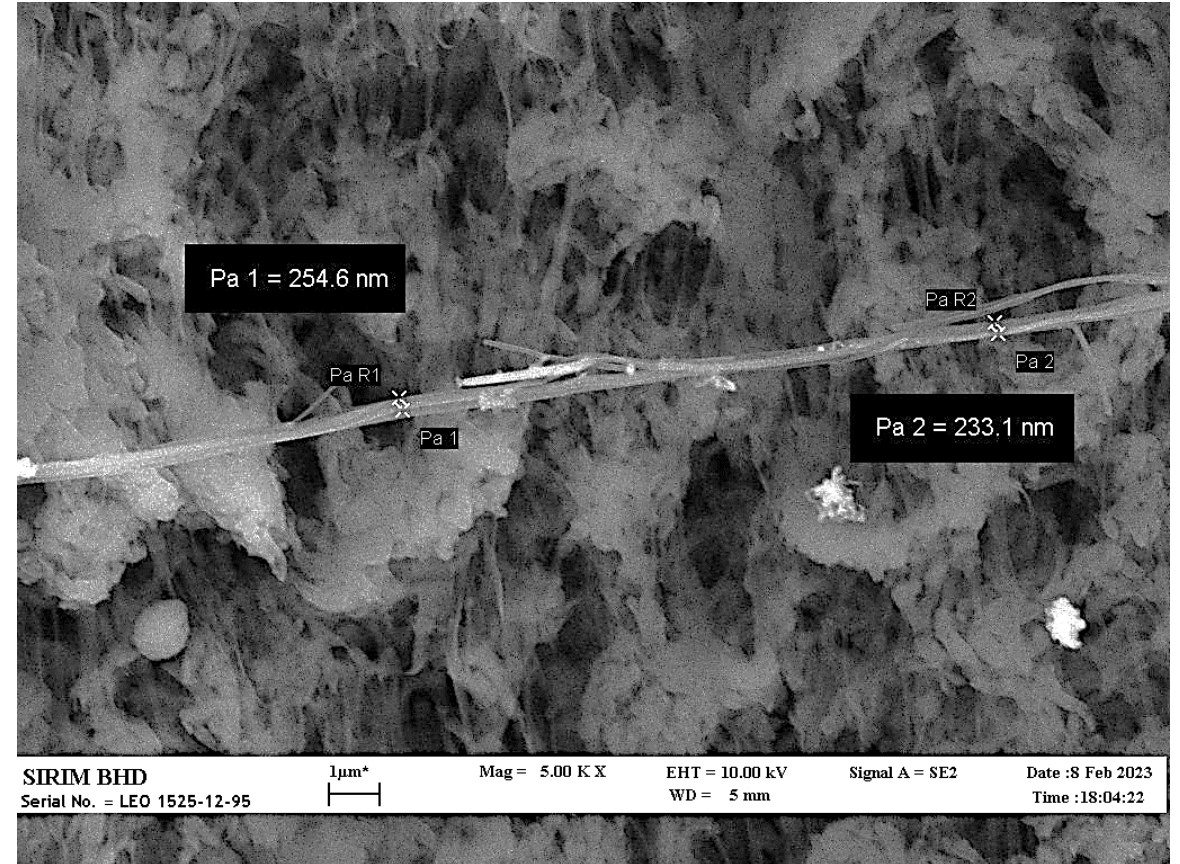
5000 x, chest position

Size in length = 2 to 10 micron

## Microscopic Analysis by SEM – Size in Diameter



10000 x, chest position



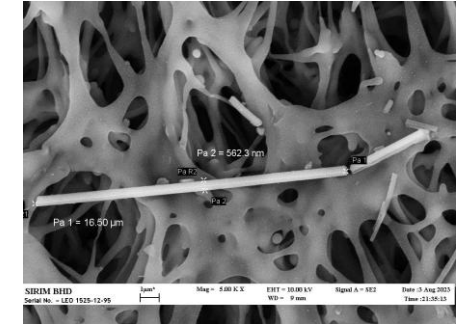
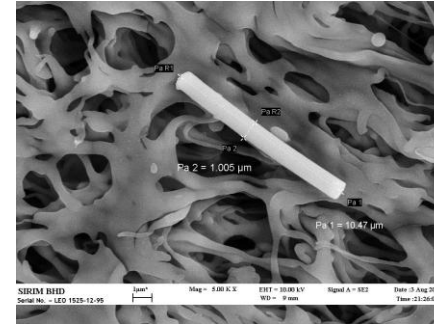
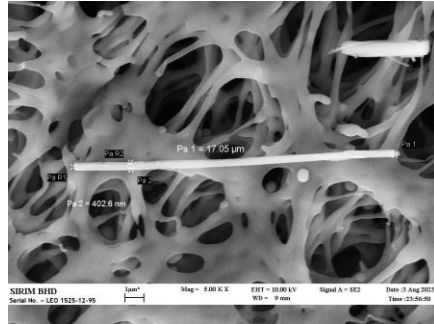
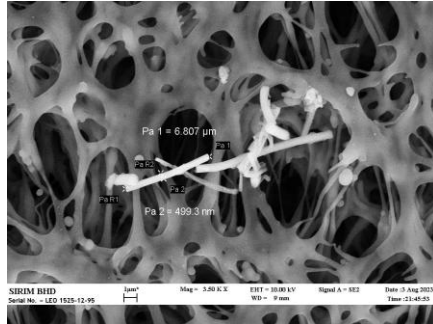
5000 x, chest position

Size in diameter = 80 to 250 nm

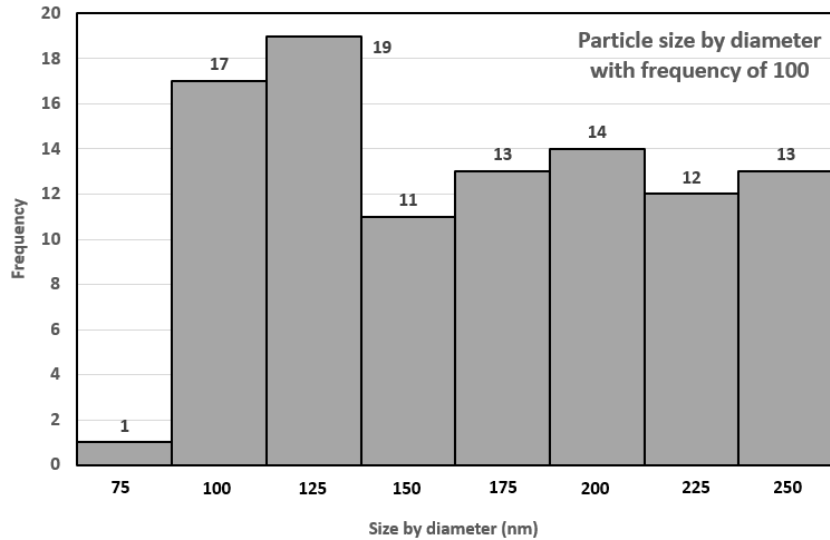
## Scanning Electron Microscopy



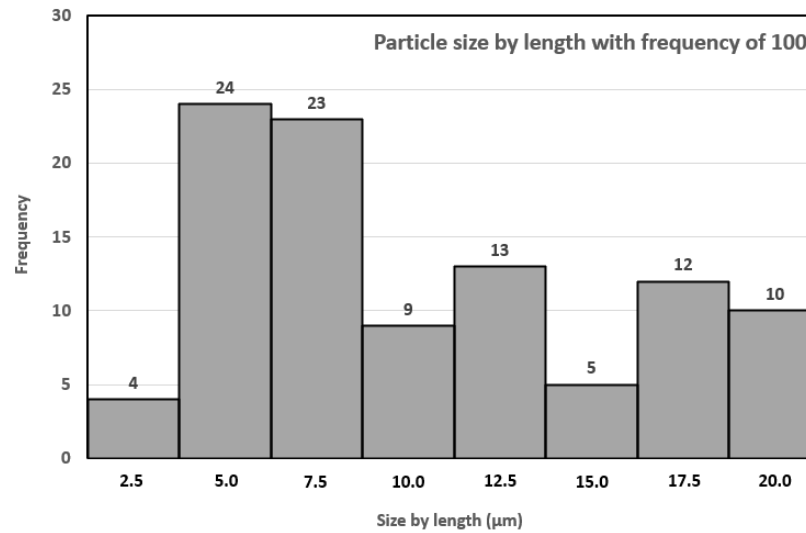
Frequency of 100 particles



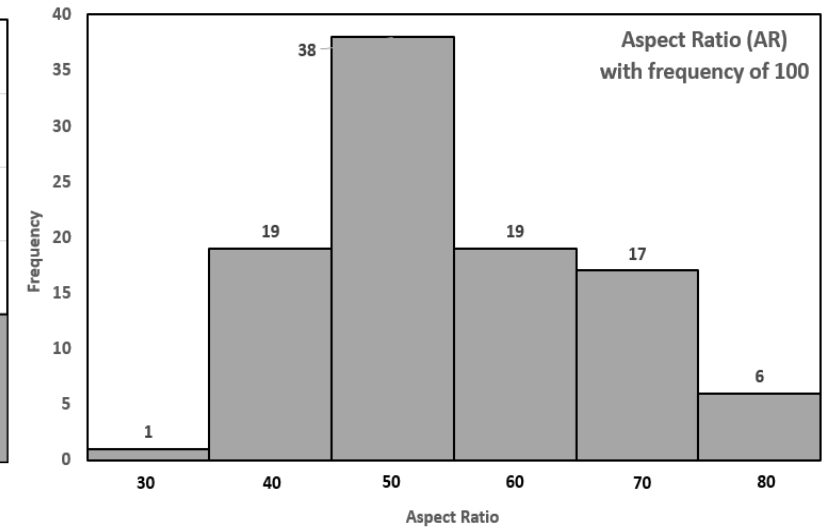
Number of particle = 100



Distribution by size by diameter

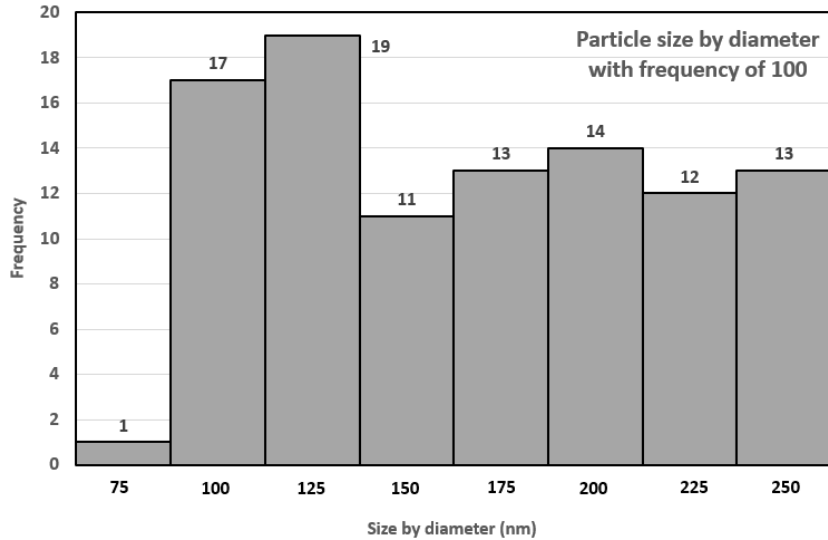


Distribution by size by length

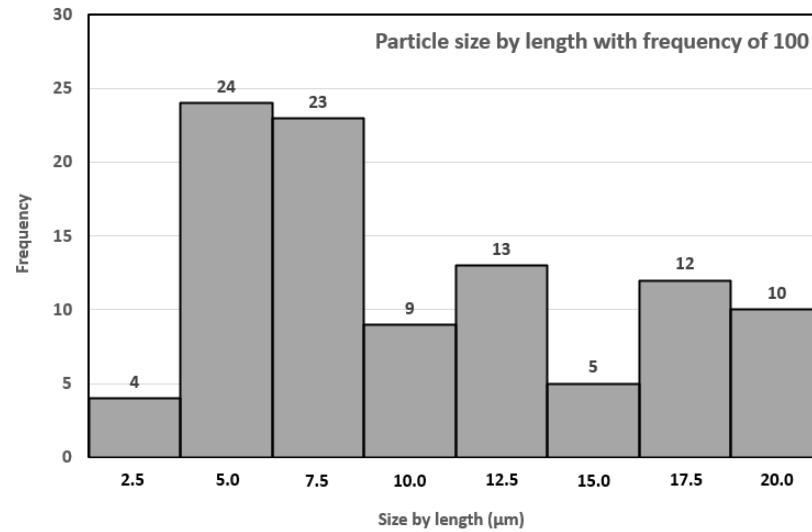


Distribution by aspect ratio

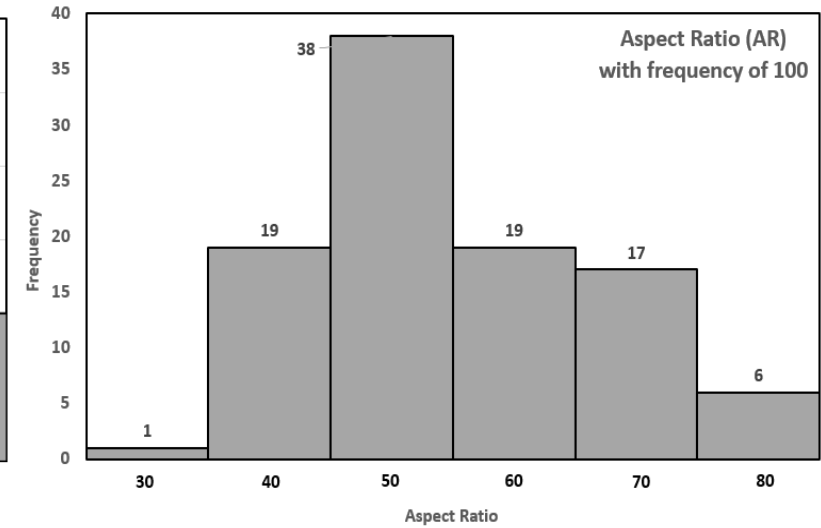
## Scanning Electron Microscopy



Distribution by size by diameter

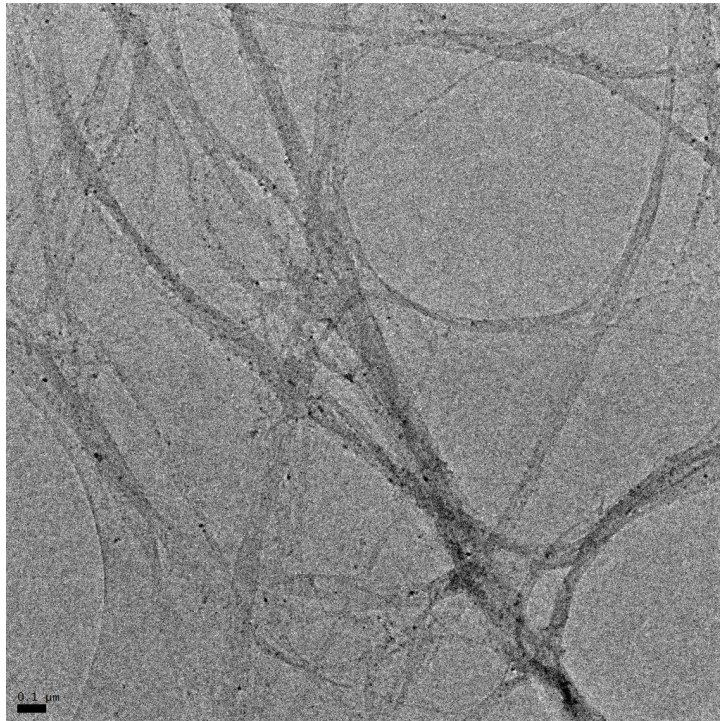


Distribution by size by length



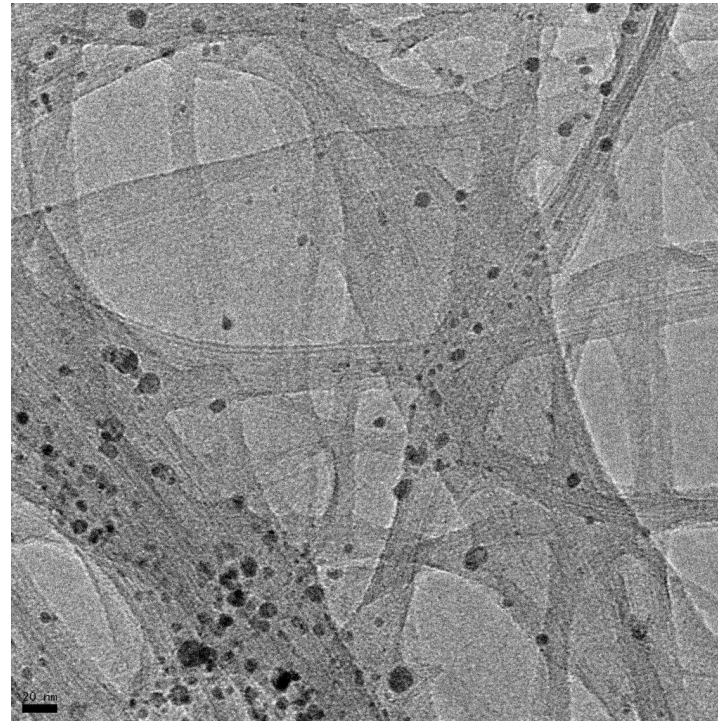
Distribution by aspect ratio

Morphology Description	Particle Size	Particle Shape
Fibrillar (sharp tube)	Size in diameter is 80 to 250 nm Size in length is 2.5 to 20 micron	Aspect ratio is between 30 to 80



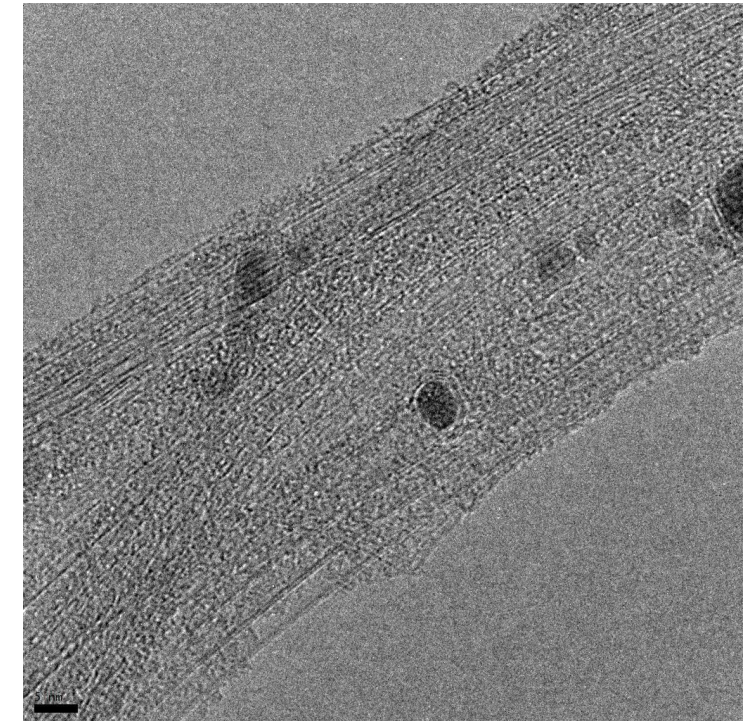
Magnification : 7 KX

**Curled-up. Non-aggregates but may agglomerates**



Magnification : 40 KX

**Parallel overlapping. Non-aggregation**

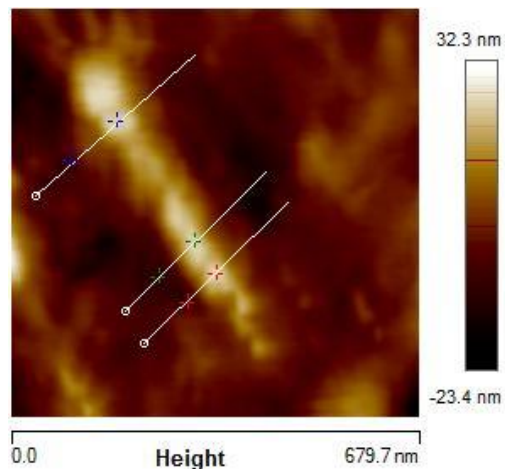


Magnification : 145 KX

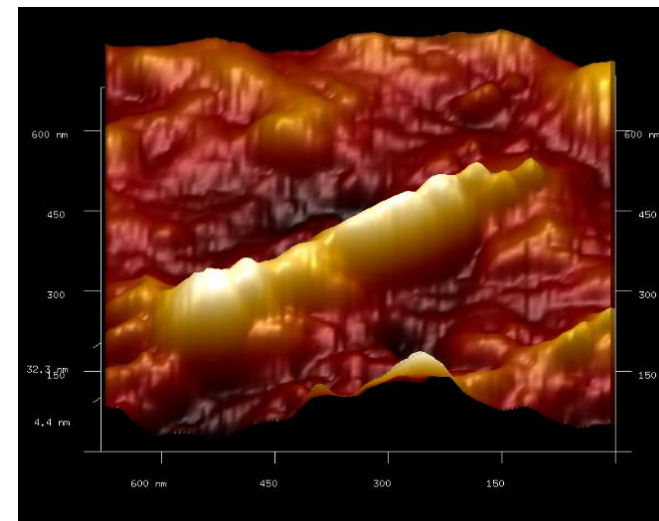
- **Multiwall carbon nanotube**
- **Diameter – 80 nm**
- **Between plane – 5nm**



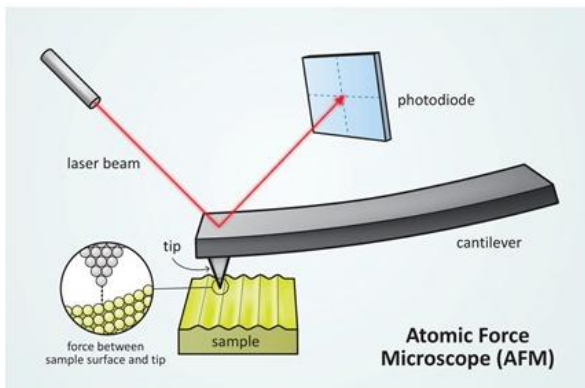
Bruker Innova



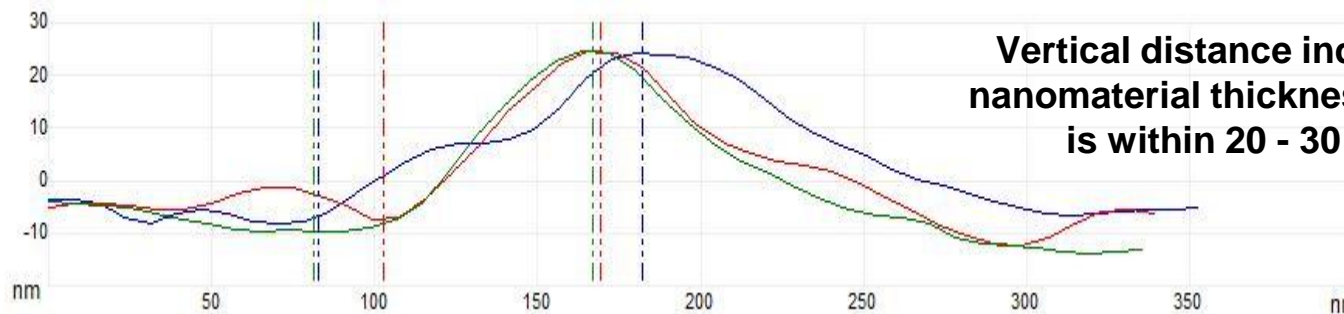
2D line profile



3D imaging



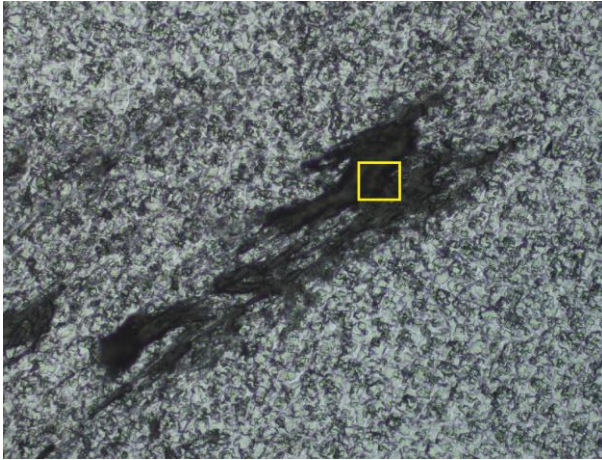
Atomic Force Microscope (AFM)



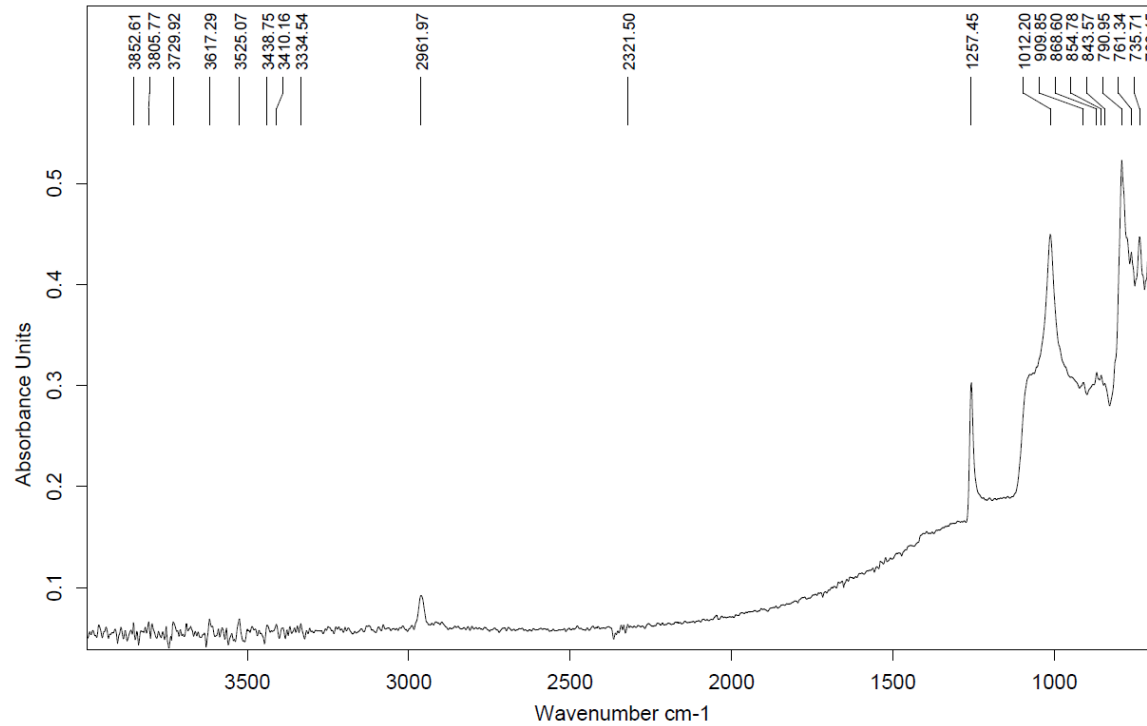
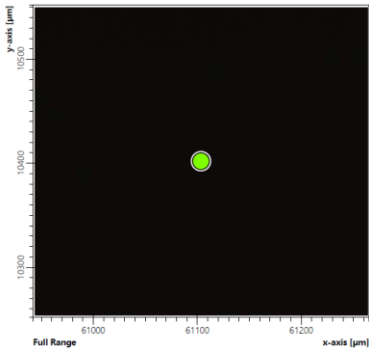
Vertical distance indicating nanomaterial thickness/radius is within 20 - 30 nm



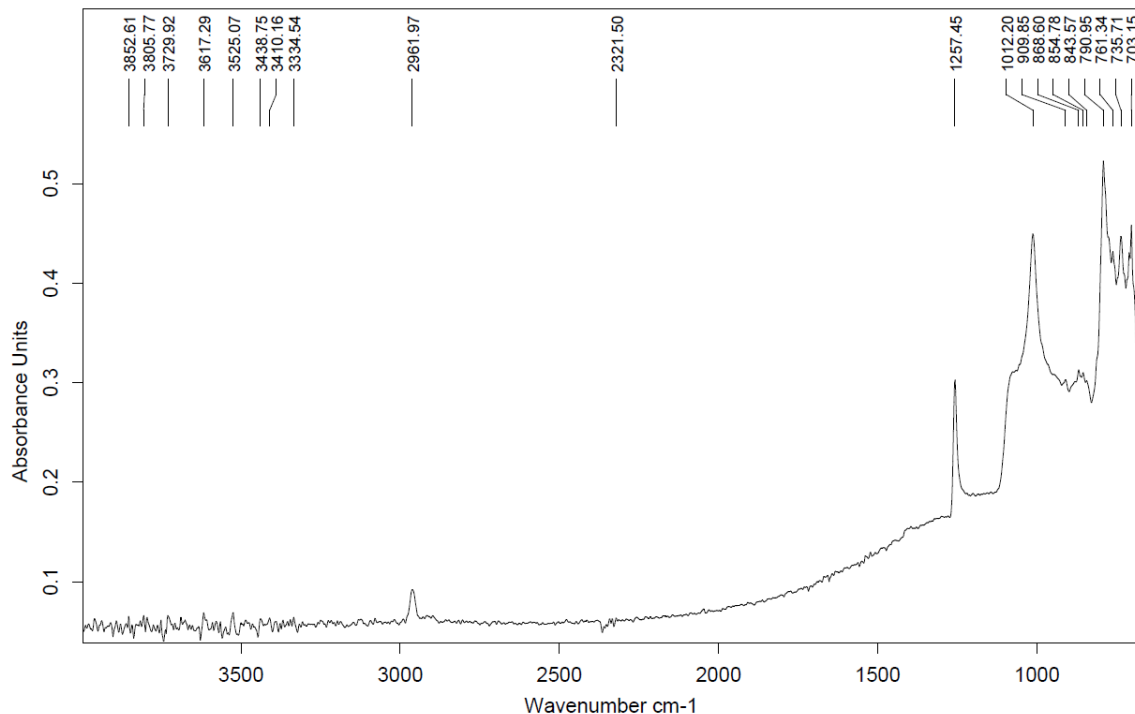
## Chemical analysis for carbonaceous identification



Point of FTIR measurement on deposited filter



FTIR spectrum of nanoparticle collected at thermal treatment area



FTIR Vibrational		
Wavenumber Range (cm <sup>-1</sup> )	Bond	Type of vibration
2961.97	CH <sub>2</sub>	Symmetric and asymmetric stretching
1257.45	CH <sub>2</sub>	Bending
1012.20	C-O	Symmetric stretching for (alcohol, carboxylic, anhydrides)
909.85 – 703.15	C-H	Out of plane stretching for aromatic

**FTIR spectrum of nanoparticle collected at specific areas of Carbon Fiber Laboratory**

- The spectra and functional groups indicated that the carbon are
- Within C=C due to presence of hybridization of sp<sup>2</sup>
  - Having out of plane C-H, possible a wrap-up graphite structures

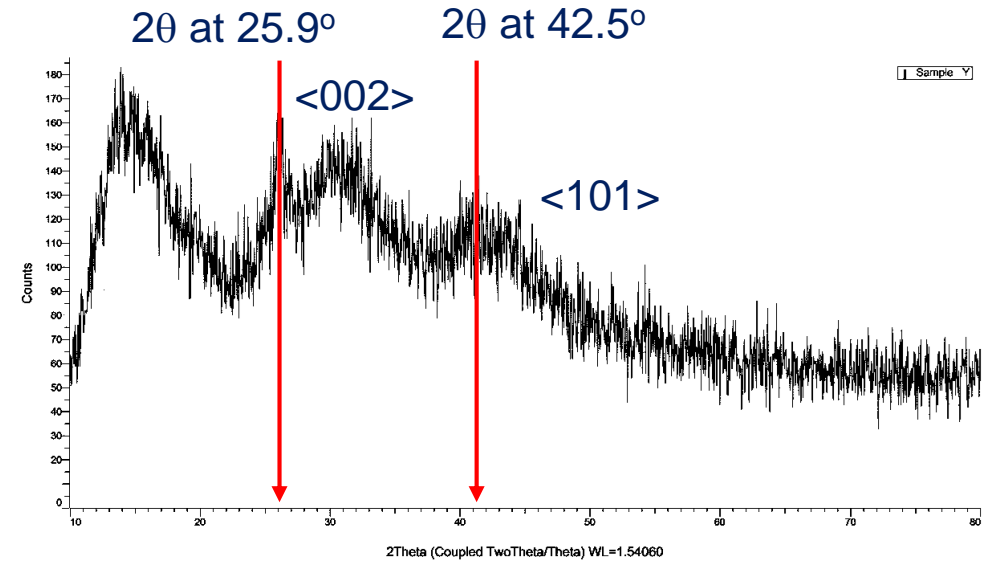
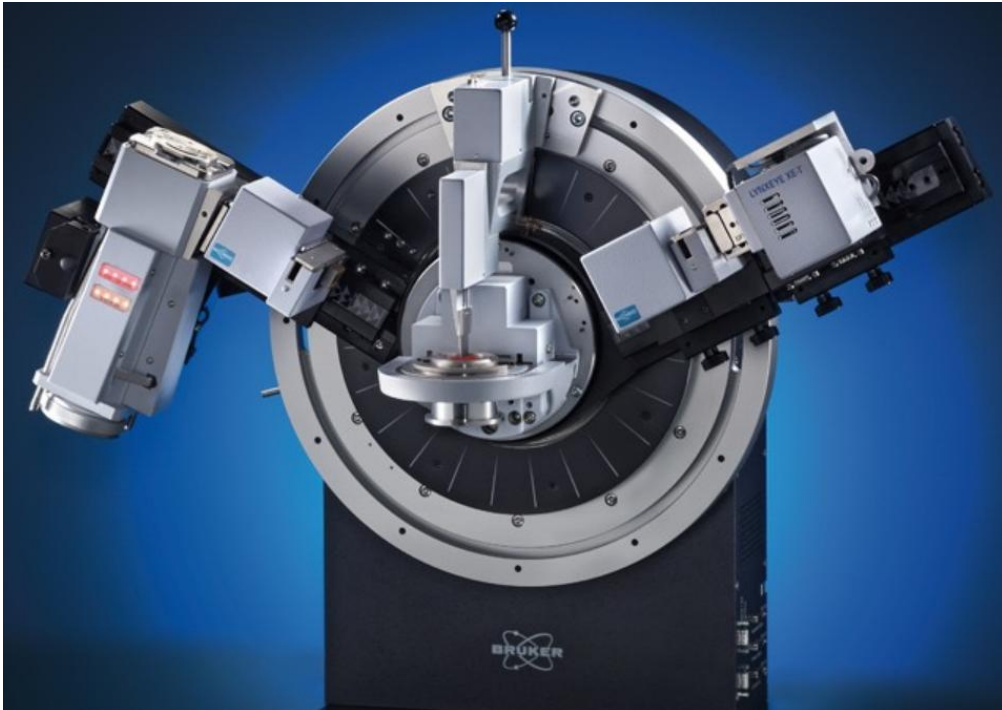


Chemistry

FTIR

XRD

EDS



XRD diffraction spectra of sampled deposited nanomaterial

XRD patterns for CNTs are characterized by;

- Graphite-like peak at diffraction plane of <002> and <101>
- A sharp peak at diffraction  $2\theta$  angle of  $25.7^\circ$
- A broad reflection peak at diffraction angle of  $42.9^\circ$

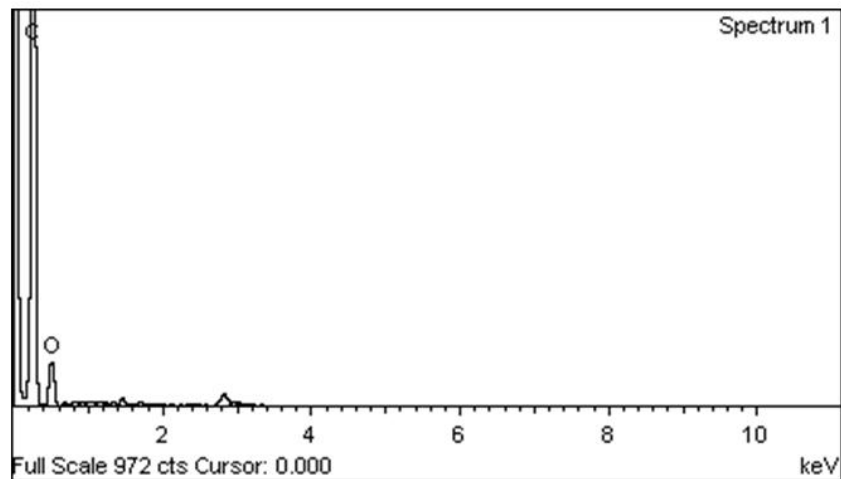
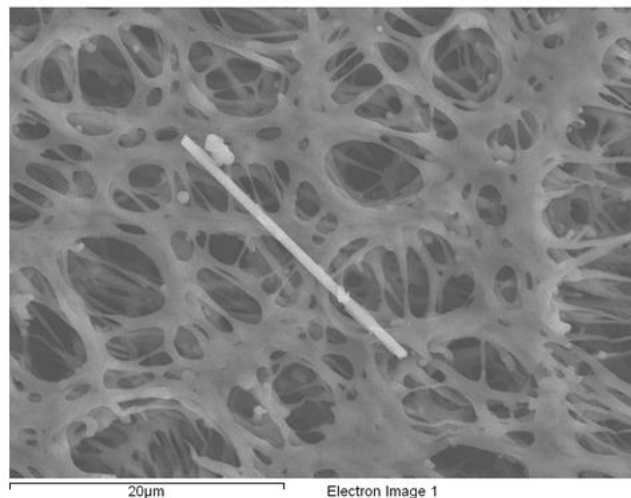
**The diffraction peaks at  $2\theta$  of  $25.9^\circ$  and  $42.5^\circ$  confirming that the carbon allotropes crystal are in cylindrical form – CNTs and/or CNFs**

Chemistry

FTIR

XRD

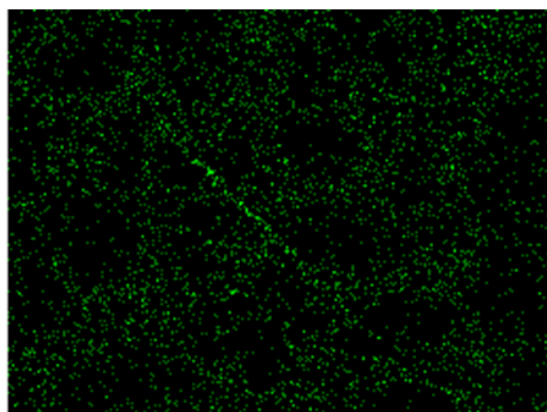
EDS



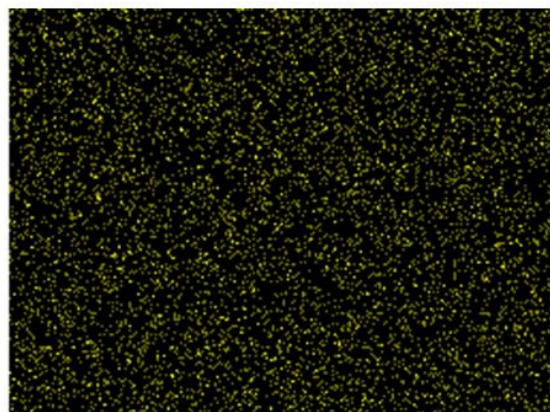
Chemical analysis  
- for elemental and impurity disorder

Mainly C, O and Si

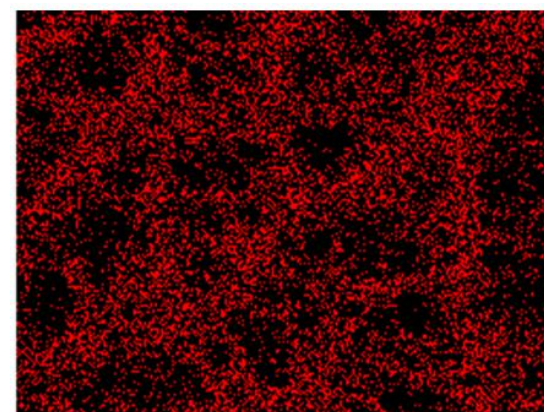
- C and O from the nanoparticles
- Si from the substrate/filtrate



C K $\alpha$



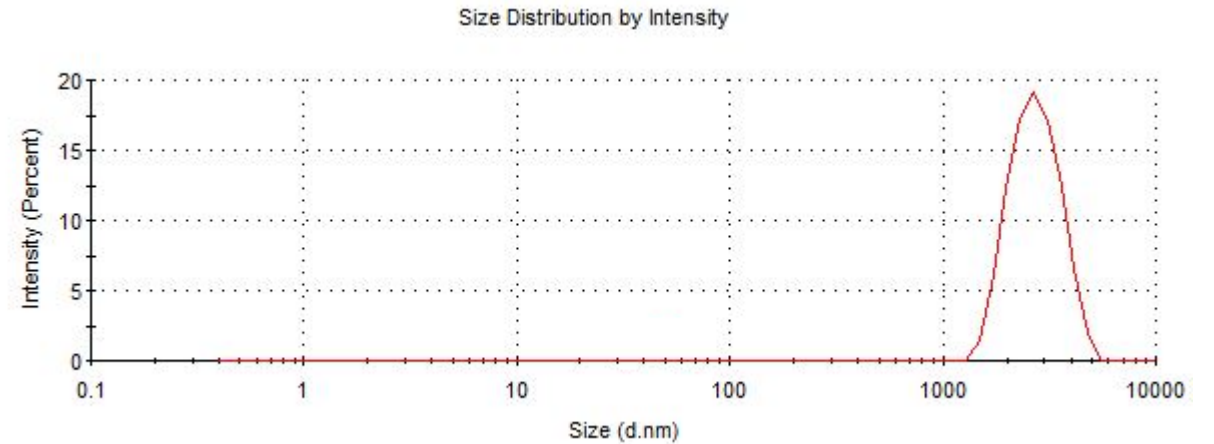
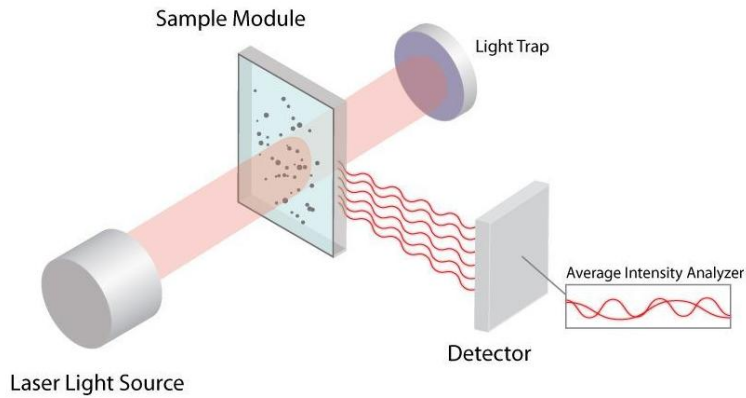
O K $\alpha$



Si K $\alpha$

Determination by  
point on the fiber

# Physicochemical : Physical : Dynamic Light Scattering

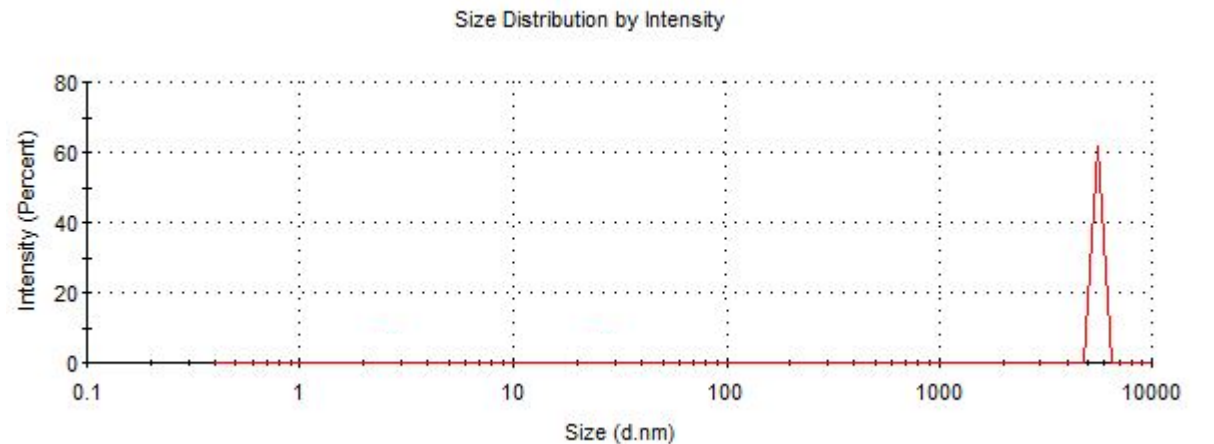


DLS spectrograph on material synthesis area



Dynamic Light Scattering

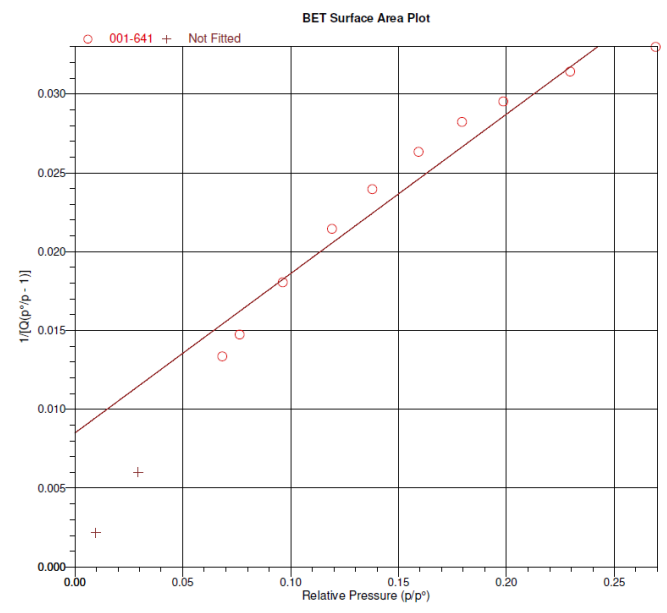
Physical analysis for nanoparticle size distribution



DLS spectrograph on thermal treatment area



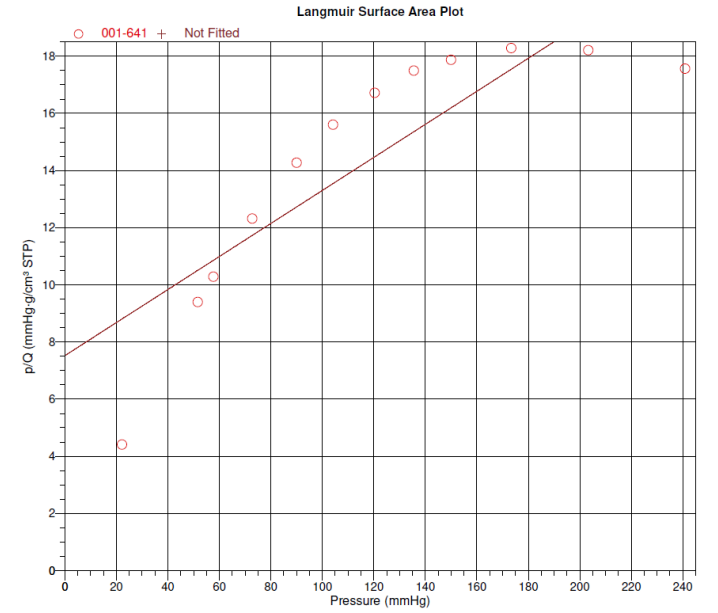
**Brunauer-Emmett-Teller Analyser**



**BET Surface Area Plot**

**Surface Area**

Single point surface area at  $p/p^\circ = 0.318896531$ : 40.6431 m<sup>2</sup>/g  
BET Surface Area: 39.6991 m<sup>2</sup>/g  
Langmuir Surface Area: 75.2835 m<sup>2</sup>/g

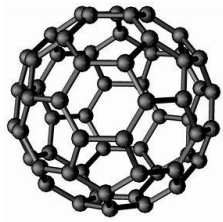


**Langmuir Surface Area Plot**

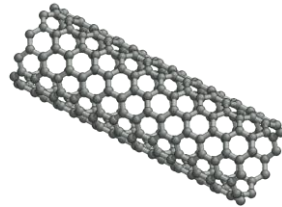
**Pore Size**

Adsorption average pore diameter (4V/A by BET): 0.70520 nm  
Desorption average pore diameter (4V/A by BET): 13.29948 nm  
BJH Adsorption average pore width (4V/A): 5.1660 nm  
BJH Desorption average pore width (4V/A): 5.0752 nm

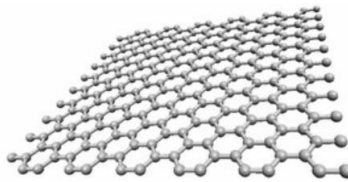
## IDENTIFY GROUP



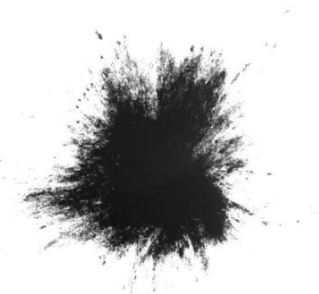
Fullerene



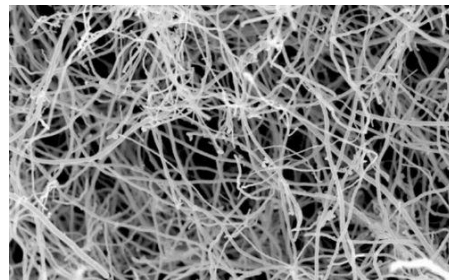
Carbon nanotubes  
(CNTs)



Graphene



Carbon black



Carbon nanofiber  
(CNFs)

From study on the manufacturing process, raw material in use and final desired product outcomes, exposure on carbonaceous nanoparticle shall be possibly comes from three main allotropes;

- Fullerene
- Carbon nanotubes (CNTs)
- Carbon nanofiber (CNFs)

However based on finding from sampling, only 2 allotropes present;

- CNTs
- CNFs

# Exposure Identification & Categorization

## From Physicochemical Characterization & Analysis

**CLSM**

**TEM**

Size in diameter is 80 to 250 nm  
Size in length is 2.5 to 20 micron  
Aspect ratio is between 30 to 80

**SEM**

**AFM**

**FTIR**

collected carbonaceous compound having high C=C in composition with sp<sup>2</sup> hybridization

**XRD**

having crystal structure quite similar to CNTs

**EDS**

Mainly consist of C and O

**DLS**

Sedimentation and agglomeration restricted measurement

**BET**

Surface area of 75.2 m<sup>2</sup>/g (Langmuir)  
Small pore size of 5.1 nm (BJH calculation)

## Categorization

**CHEMISTRY**

Confirming that the collected carbon allotropes can be categorized into CNTs and CNFs, geometric arrangement for fullerene is not detected

**MICROSCOPY**

**Physical**

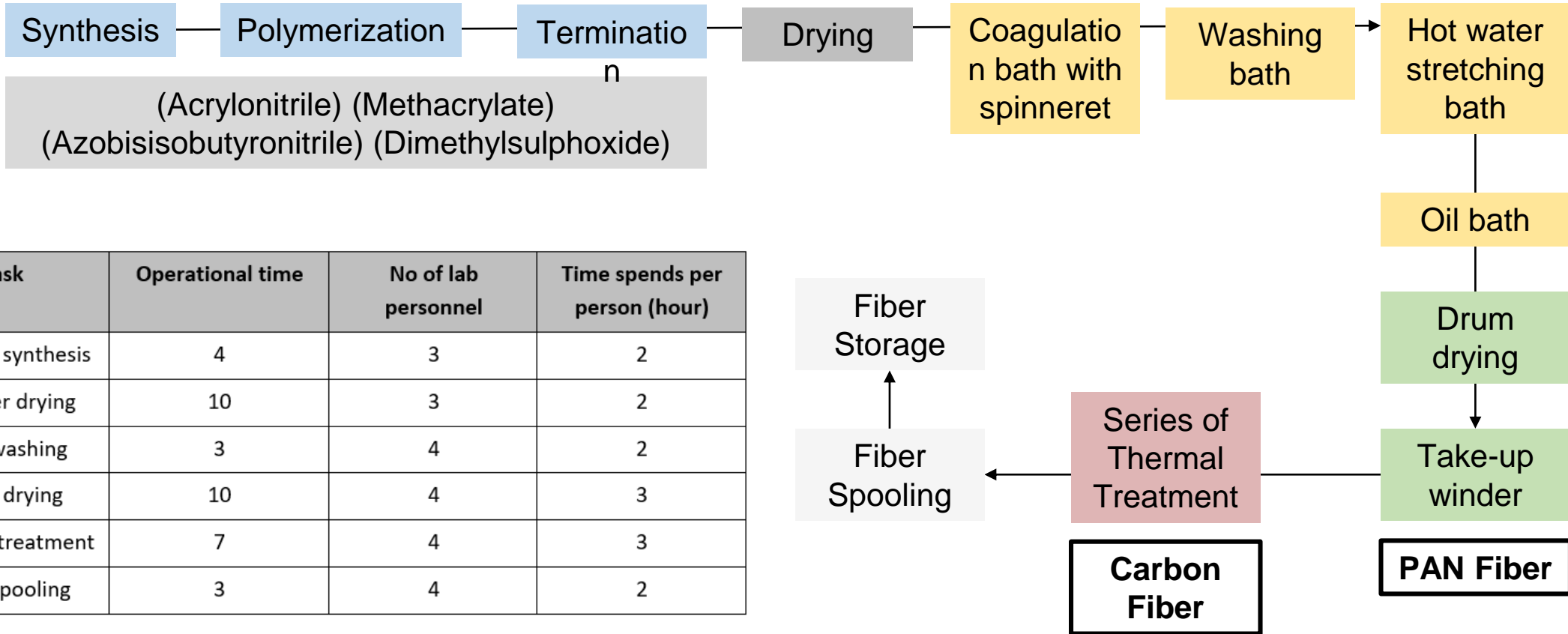
Confirming that the collected carbon allotropes can be categorized into CNTs (by diameter) and CNFs (by diameter length)

# Questionnaire & Walkthrough



## Questionnaire & Walkthrough

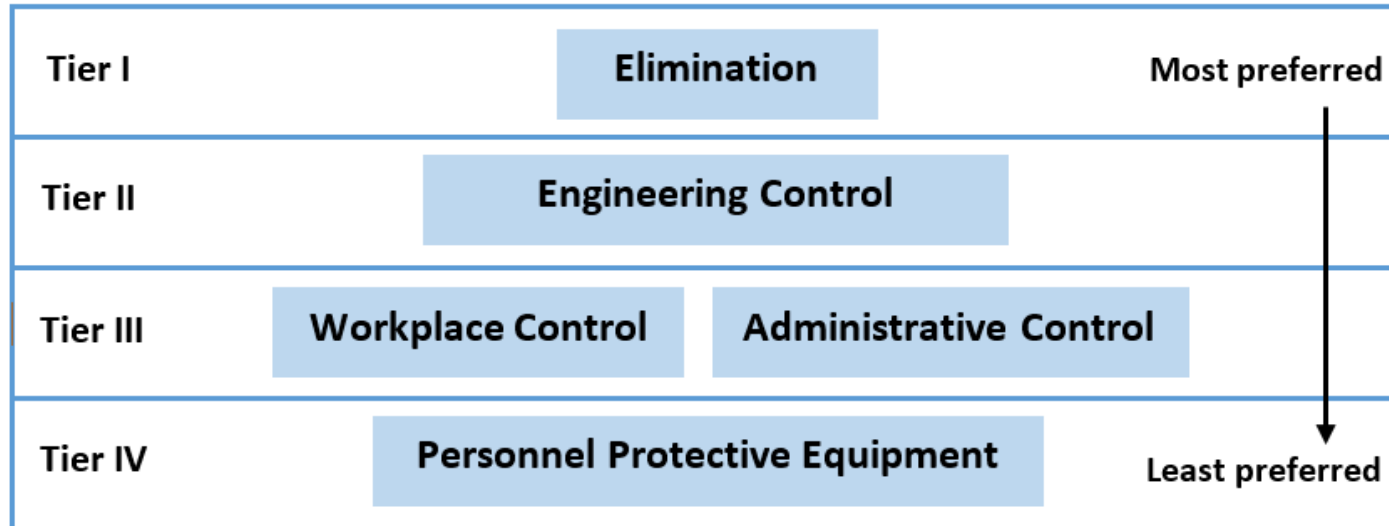
All CF Fabrication Process



task	Operational time	No of lab personnel	Time spends per person (hour)
Material synthesis	4	3	2
Polymer drying	10	3	2
Bath washing	3	4	2
Drum drying	10	4	3
Thermal treatment	7	4	3
Fiber spooling	3	4	2

# Approach on Control Measures

## Interview & Walkthrough



Department of Occupational  
Safety & Health

Guidelines on Control and Safe  
Handling of Nanomaterials 2018



Tier I	<b>Elimination</b>	Most preferred
Tier II	<b>Engineering Control</b>	
Tier III	<b>Workplace Control</b> <b>Administrative Control</b>	
Tier IV	<b>Personnel Protective Equipment</b>	Least preferred

## Tier II Engineering Control

- Ventilation - eliminate congestion
- Detector for hazardous gases



Fan and exhaust fan



Gas detector for HCN

# Control Measures

Tier I	Elimination	Most preferred
Tier II	Engineering Control	
Tier III	Workplace Control    Administrative Control	
Tier IV	Personnel Protective Equipment	Least preferred

## Tier III Personnel Protective Equipment (PPE)



protective  
clothing



safety  
eyewear



respirator



glove



hard hat



Safety boot

# Control Measures

## Tier III Personnel Protective Equipment (PPE)



*DELTA PLUS DT117 – DELTATEK 5000 coverall with elasticated with hood*



slim safety goggle

Safety Eyewear



*Safetyware Chem-Pro variable flock lined nitrile glove*



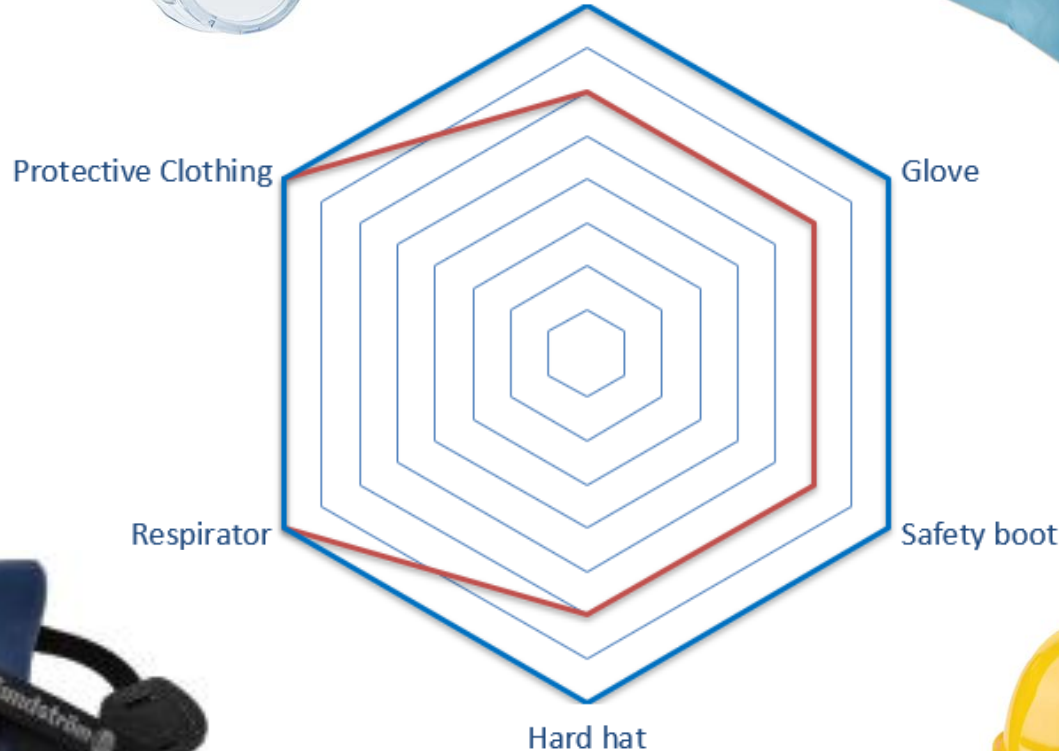
*SN101KP RHINO shoe sneaker series safety shoe*



*HDP01AP Safetyware Explorer safety helmet*



*Safetyware FFP2 vertical fold-flat OV/AG particulate respirator with valve, with activated carbon to filter nuisance level organic vapor and acid gases*



— Required by NaRA — Lab Assessment

# Control Measures

Tier I	Elimination	Most preferred
Tier II	Engineering Control	
Tier III	Workplace Control    Administrative Control	
Tier IV	Personnel Protective Equipment	Least preferred

**Tier III**  
**Workplace Control & Administration Control**



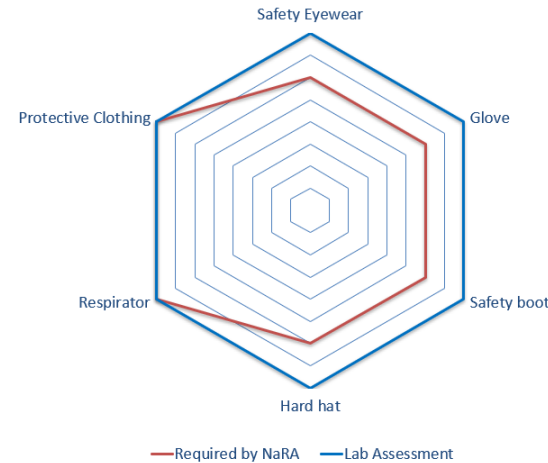
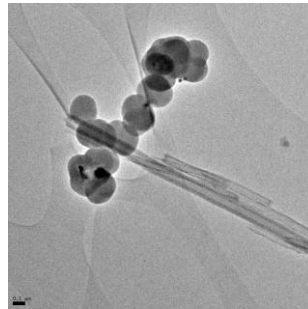
- Scheduled work place inspection, waste management
- Routine inspection on critical equipment and process

- **Sampling on exposure of carbonaceous nanomaterial regarding to occupational safety and health has been performed within Carbon Fiber Fabrication and Processing Laboratory**
- **Physicochemical on the basis of microscopy, chemical analysis and physical properties has been executed toward definition of the physicochemical exposure**
- **Data on particle size, shape, agglomeration properties, chemical identification and carbonaceous hybridization has been successfully define**
- **Control measures on the exposed nanomaterial has been executed where particular measures have been carried out toward exposure control**

# Quest for Fantastic Integration of UN SDGs in ESG



Sustainability performances and harmonization  
- scopes, boundaries, indices & ranking



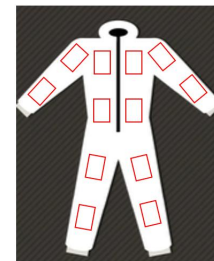
MaRINA 2.0 – Research Focus Area in Nanomaterial



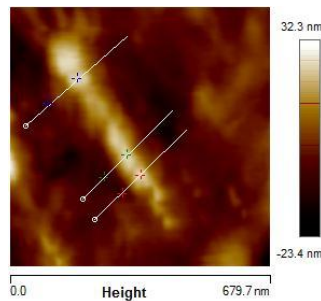
Department of Occupational Safety & Health

Guidelines on Control and Safe Handling of Nanomaterials 2018

OSH Framework



Controlled measures in nanomaterial



Data :  
Nanomaterial exposure classifications



Learn : Re-Learn : Co-Learn



*Project Title :*  
***Physicochemical Exposure Assessment on Carbon Fiber for Nanomaterial Processing Laboratory***



support of the  
**National Institute of Occupational Safety and Health (NIOSH)**  
grant [(03.16/03/ PHYSICOCHEMICAL(E)2021/01)



**COSH**  
2024  
24<sup>th</sup> CONFERENCE AND  
EXHIBITION ON  
OCCUPATIONAL  
SAFETY AND HEALTH

**SCICOSH**  
6<sup>th</sup> SCIENTIFIC CONFERENCE ON OCCUPATIONAL SAFETY AND HEALTH



**Thank you**

*Best Partner for Innovation*



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