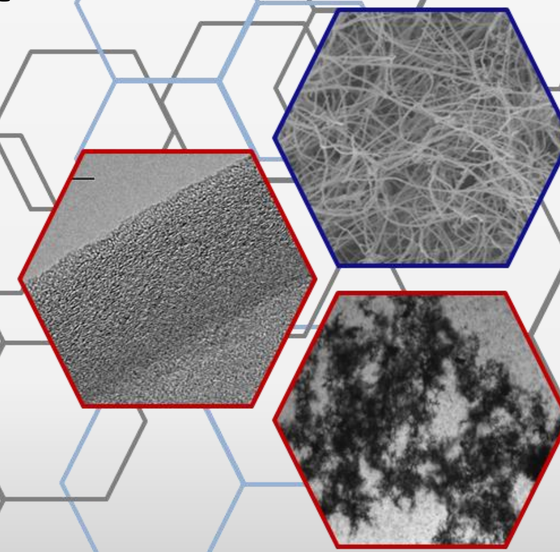
Microwave synthesis of graphene decorated carbon nanotubes for stray light suppression



Mirror Tech SBIR/STTR Workshop |November 5, 2018|

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Applied Sciences Inc

141 W. Xenia Ave

Cedarville, Ohio

Overview

- Company Background
- Problem Statement
- Program Goals
- Approach
- Results
- Discussion

Company Chronology

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- **1984:** Applied Sciences was founded in Cedarville, OH to research advanced carbon based materials
- **1995:** ASI secured exclusive license for GM patents for GM's VGCF technology
- **1995 – 2000:** ASI lead NIST ATP Project to develop VGCF composite technology for automotive composite applications
- **1996:** PPI subsidiary incorporated in Cedarville to manufacture, market VGCF "Pyrograf-III" carbon nanofiber
- **2002:** PPI accepted strategic investment and spun off from ASI
- **2010:** PPI received ISO 9001 Certification
- **2011:** Received Consent Order from EPA for sale of CNF for domestic, commercial applications

Facilities in Cedarville, OH

ASI has 14,000 sq. ft lab and office space with a >40,000 sq. ft. manufacturing affiliate, Pyrograf Products directly across the street.

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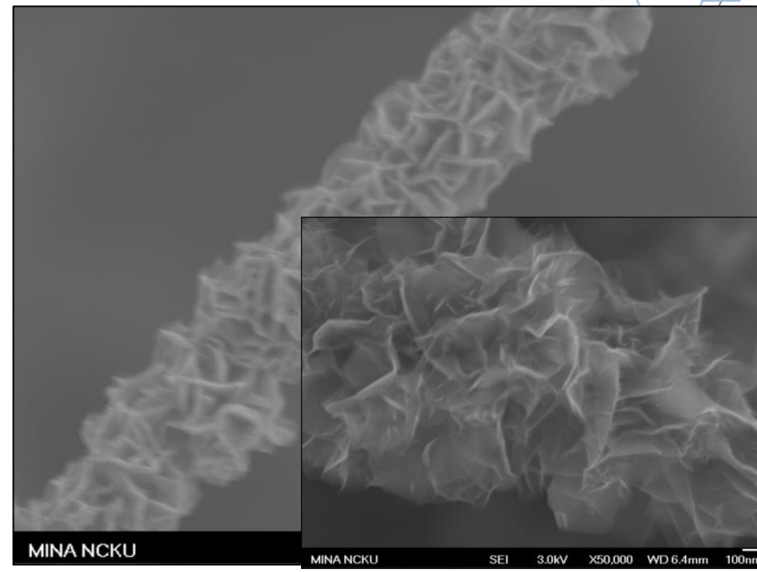
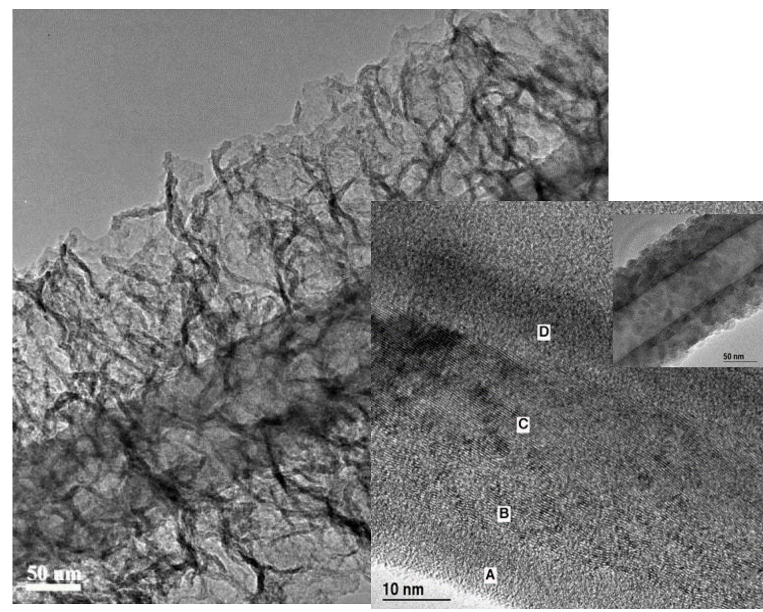
R&D of novel carbon forms and vertical integration





Pyrograf Products, Inc

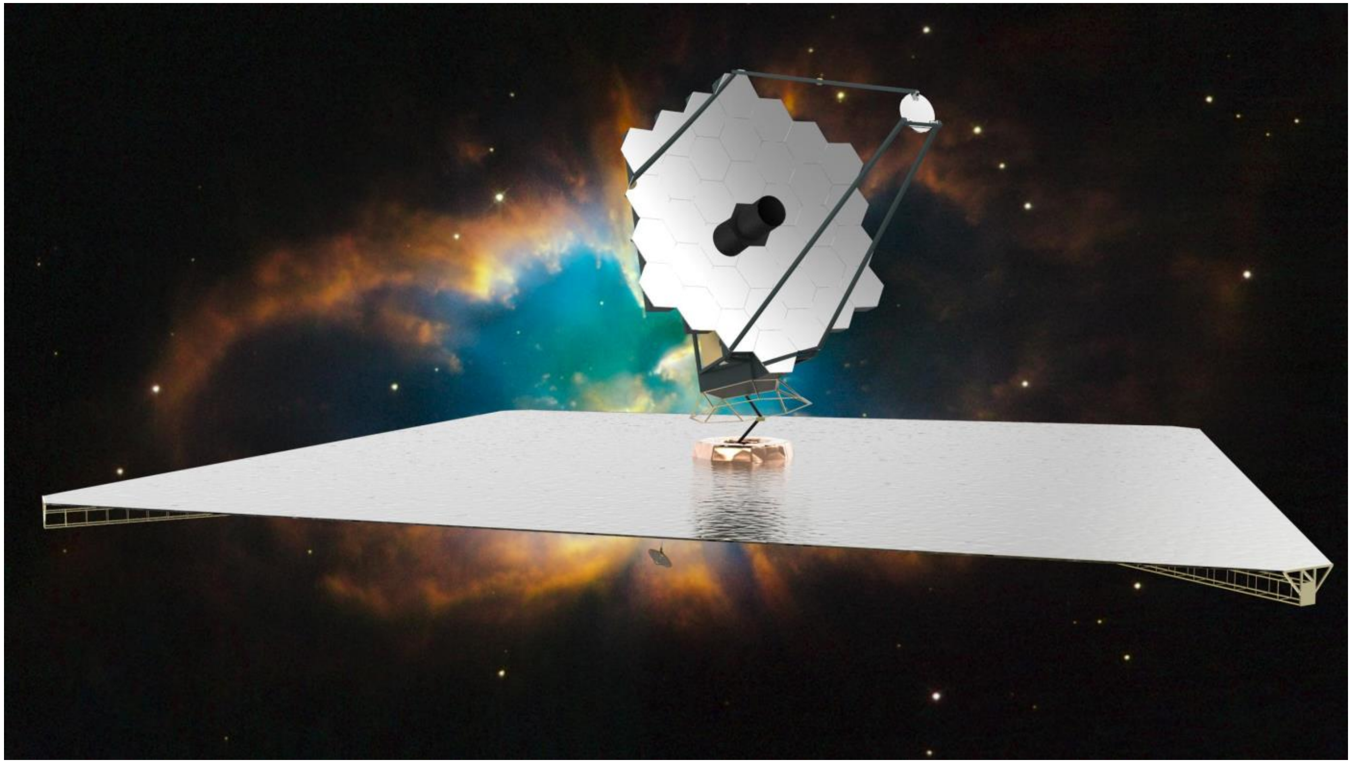
PPI has 70,000 lb / year capacity with room to expand to 1M lbs. / year

Current prices vary from: $174/lb to $332/lb

Far-term price will approach carbon black.

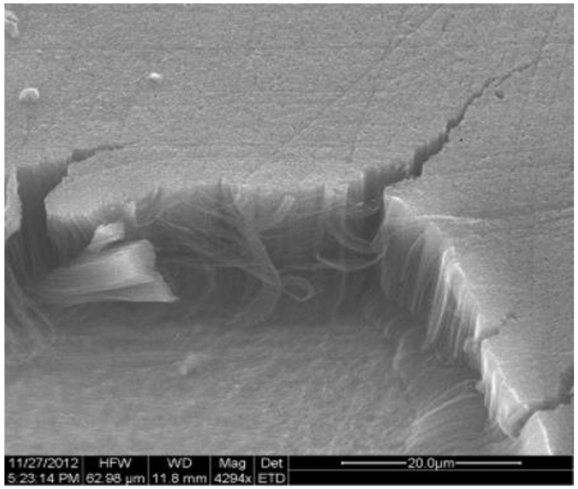
www.pyrografproducts.com

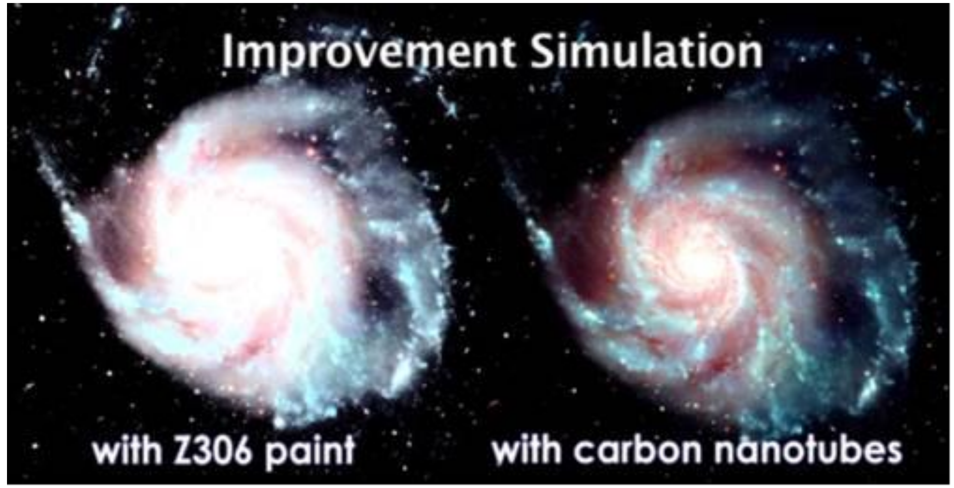
Problem Statement



Highly ambitious NASA missions impose very stringent requirements for sensors, and thus for highly absorbing materials to reduce stray light contamination. New absorptive materials are needed to support future sensors which are far beyond today's capability.

Current State of the Art





Current state of the art stray light treatments, such as the Z306 flat black polyurethane, results in approximately 4% of stray light being reflected.

Dr. Hagopian's group at NASA Goddard Space Flight Center (GSFC), developed a carbon nanotube coating that is 10 times more efficient suppressing light than the Z306. The developed technology consists of growing vertically orientated MWCNT films onto silicon and titanium.

Surrey Nanosystems, in the UK, developed a method that can grow vertically aligned nanotubes arrays at 400 °C, trademarked as Vantablack. A coating featuring the same nanomaterials was developed. Despite the incredible performance of this coating, it is quite costly and subject to export control.

1. Hagopian, J. et al. Proc. Of SPIE, 2010, 7761. DOI: 10.1117/12.864386
2. http://www.gizmodo.com.au/2010/12/why-did-nasa-create-a-material-ten-times-blacker-than-the-blackest-black-paint
3. Hagopian, J. et. al. Enhanced-Adhesion Multiwalled Carbon Nanotubes on Titanium Substrates for Stray Light Control. NASA Tech Briefs, June 2012.

Phase II Goals:

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NASA is seeking new coating technologies based on carbon nanotubes that can achieve a broadband reflectivity of less than 0.1%, have good adhesion to protective metal coatings and with superior mechanical properties to withstand launch conditions.

ASI seeks to optimize, scale-up, and commercialize room-temperature curing, high optically absorptive coatings based on carbon nanotechnology.

Polymer composites can be applied to optically flat surface via the use of multiple temporary photomasks and precision deposition. Hence avoiding the pyrolytic reactive conditions required to grow carbon nanostructures in-situ.

Graphene has been identified as the best possible material for absorbing optical light and reducing the total hemispheric optical reflectance.

Why use a Polymer Coating?

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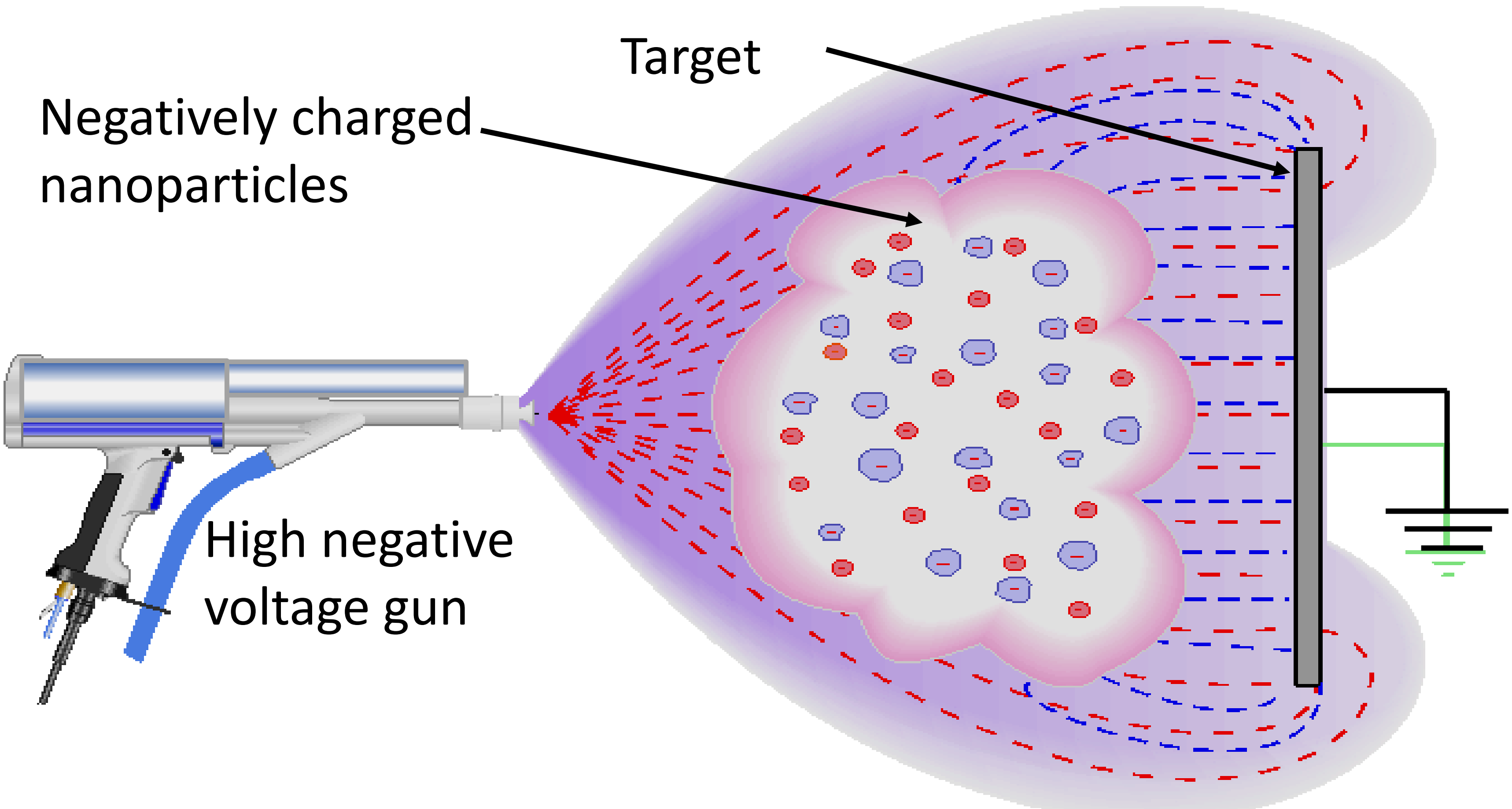
- Legacy material – Z306 is a qualified polyurethane, which makes use of carbon black for optical properties. Properties can be further improved by use of or substitution for carbon nanomaterials.
- All materials for spacecraft must survive launch environment and space environment.
- MIL STD 810
- MIL-STD-1540. Requirements for Launch, Upper-stage, and Space Vehicles.
- Survivability of free-standing nanomaterials is challenging due to adhesion issues.
- Well established distribution system, with tight quality control managing systems across the board;
- Polymeric coatings are a low cost solution to the stated problem, offering high mechanical, tribological and physical properties. Excellent batch-to-batch repeatability and reproducibility;

Electrostatic Deposition Technique



CNF Coating Development

- Tailor carbon nanomaterials geometry and surface functionality for homogeneous dispersion – essential part for optimum optical properties

- Dispersion of carbon nanomaterials in a polyurethane matrix (same base and components as Z306), using scalable high-shear dispersion methods.

- Control and monitor dispersion through – Multi-scale image analysis (MSIA)*

- Monitor and tailor the rheology and cure characteristics of Nano-filled Z306. Nano-sized materials greatly influence the flow and cure-time of polyurethanes.

- Electrostatic deposit of graphene decorated carbon nanotubes on a wet polymeric surface

*MSIA was jointly developed by ASI and WPAF Research Labs

Z306 with deposited CNFs

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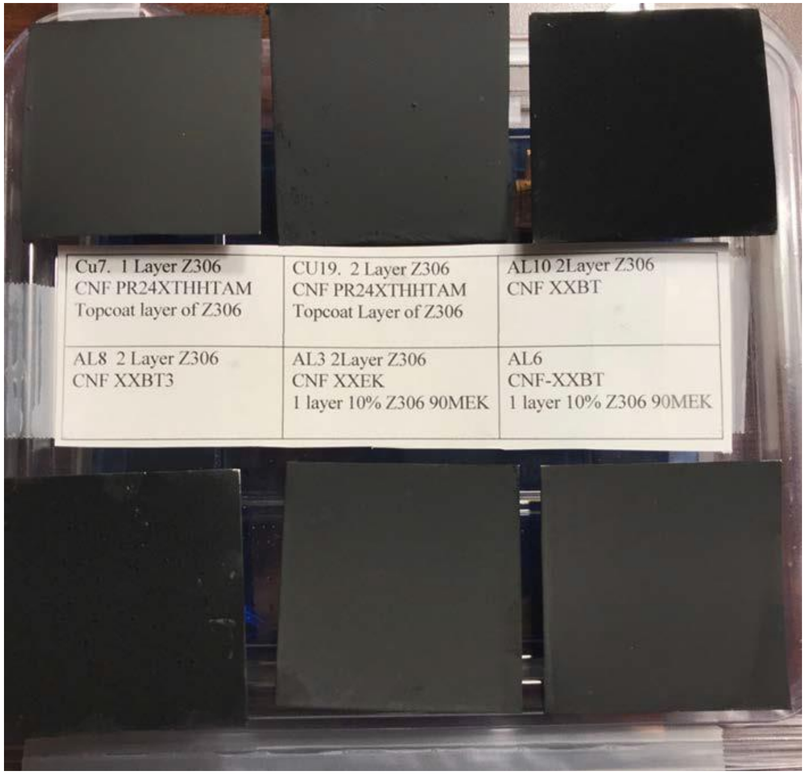
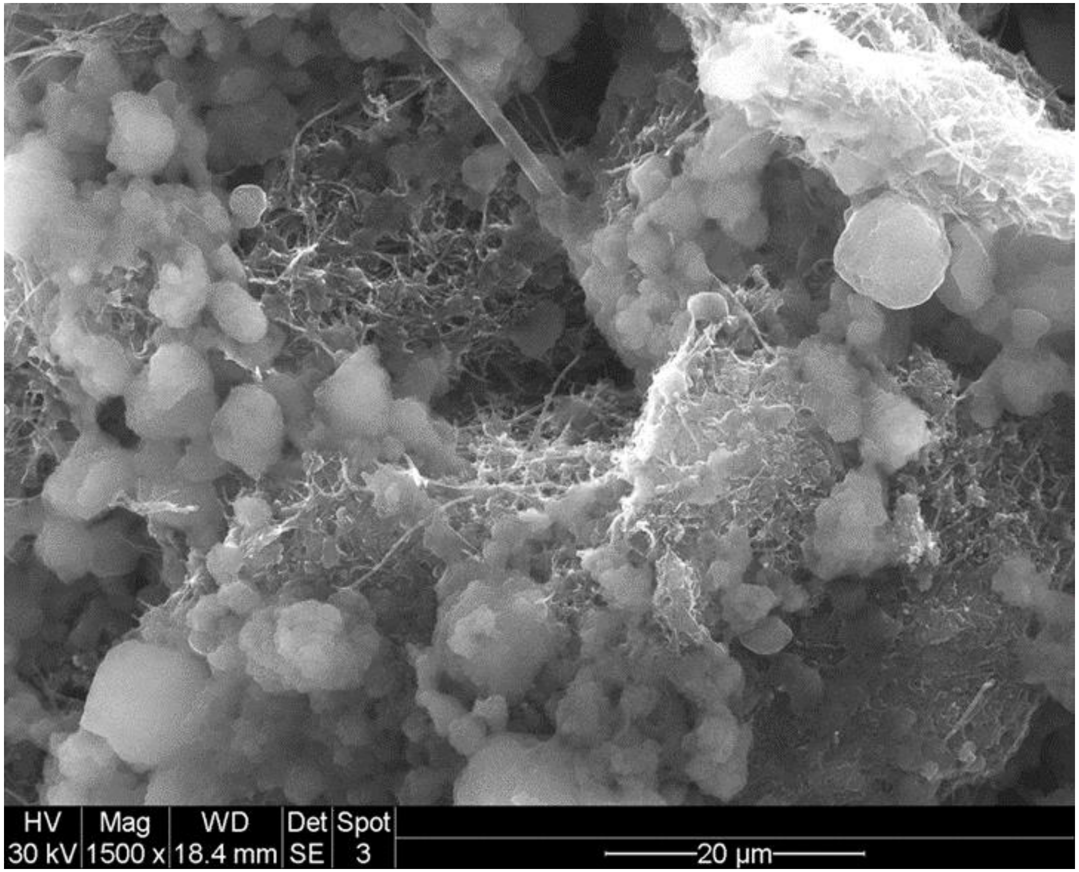


Z306 with deposited CNFs



Close inspection of the Z306/CNF/Z306 coated structure shows that nanofibers are indeed present at the surface, however, the structure afforded by the polymer appears to be more in the micron regime.

THR for Z306 and Z306 w/ deposited CNF

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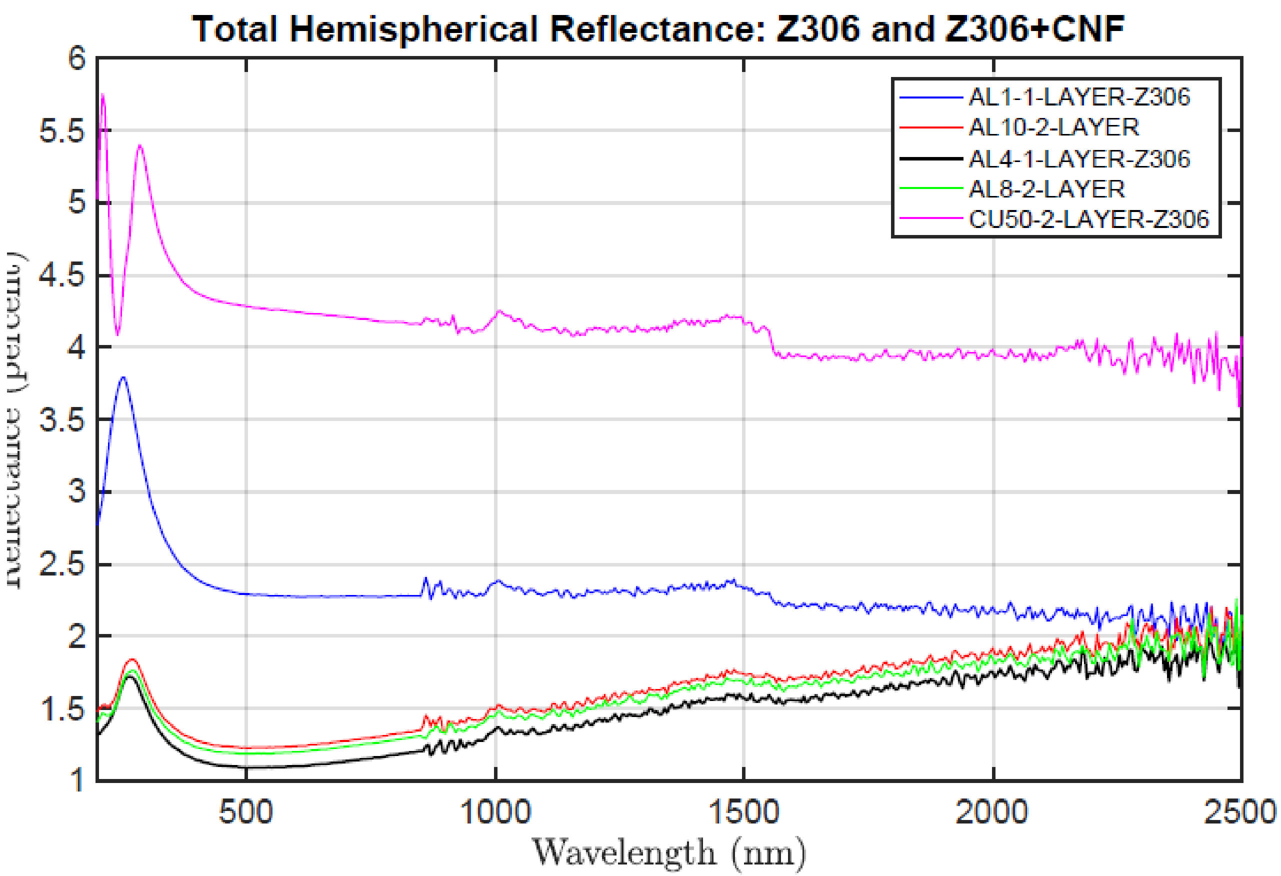

Measurements done at NASA Goddard

From a theoretical point of view, smaller diameter material results in a flatter response (PR-XX-EK appearing promising), but the absorption coefficient is all important. In that regard the BT type is clearly superior.

It can be hypothesize that functionalizing the surface can result in electronic surface states that are able to interact with incoming photons. In that regard, graphene is suggested as by far the best possible material and will be investigated in future work.

Graphene decorated carbon nanotubes coating for stray light suppression

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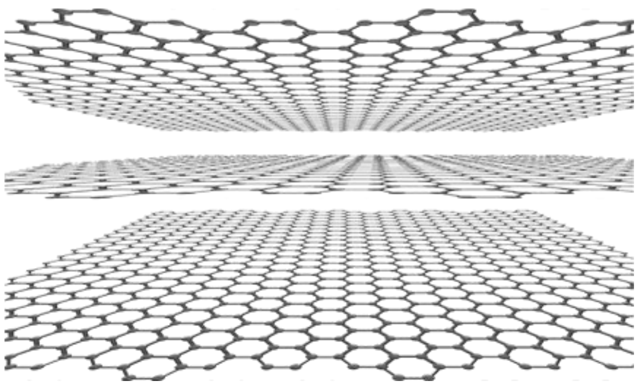
Graphene is a 2D Monolayer of Carbon Atoms



Predicted High Strength/Modulus, Zero Bandgap, High Conductivity

Extreme high mobility charge carriers on both sides of the planes---available for optical photon interactions

Nobel Prize Awarded 2011 to Keim and Novoselov

Why Graphene?

Graphene is a 2D single plane of carbon atoms. It has three neighboring atoms, bonded with a powerful sp2 bond, but 4 pi electrons. The unbonded pi electron is free to appear on either side of the plane. Hence it is extremely mobile and has a high population density.

The graphene edge plane has two up-bonded electrons.

Graphene must certainly have potential to act as a scatterer or absorber over and above alternate morphologies. Moreover, it's smallest dimension is sub-nano.

Graphene decorated carbon nanotubes coating for stray light suppression

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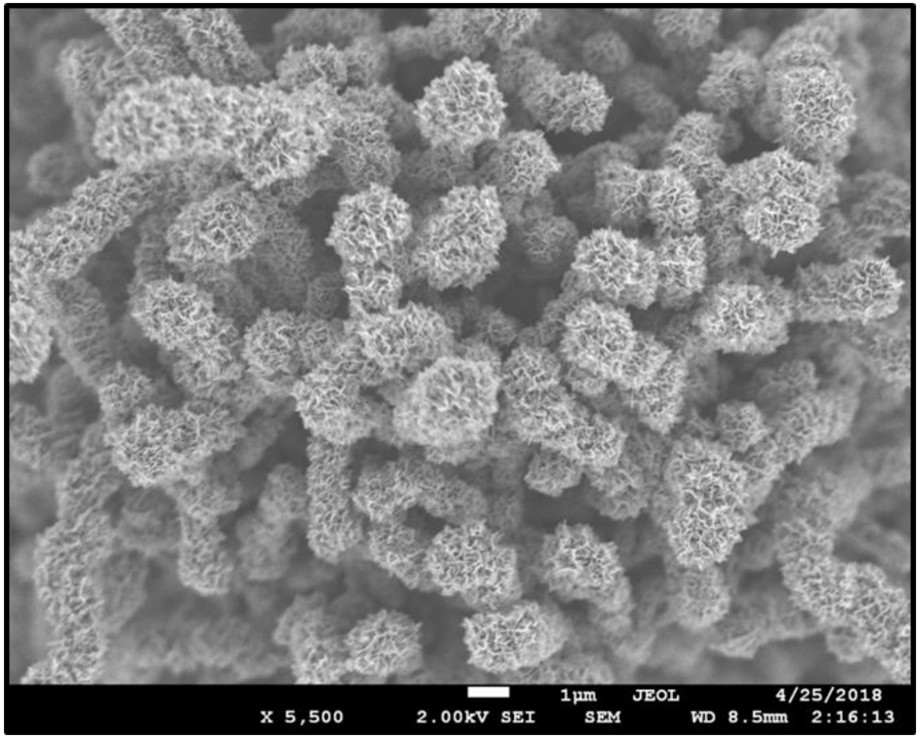
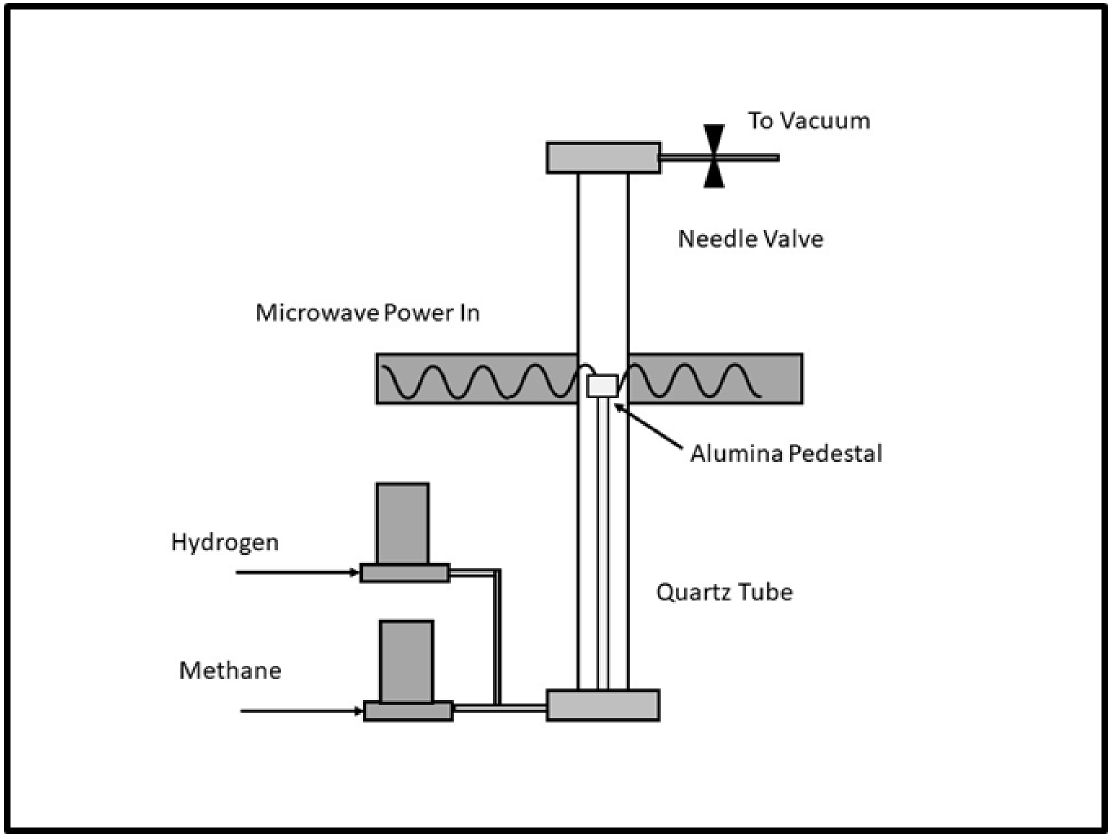


Combining the high surface area 3D framework of the CNTs coupled with the high charge density of graphene.

Create monolayer graphene absorbers, by electrostatically deposit graphene decorated carbon nanotubes on a tackified Z306 based substrate.

Microwave assisted in-situ synthesis of graphene decorated CNFs



Microwave System, based on ASTEX 1500 W system.

ASI/ASTEX Microwave Synthesis

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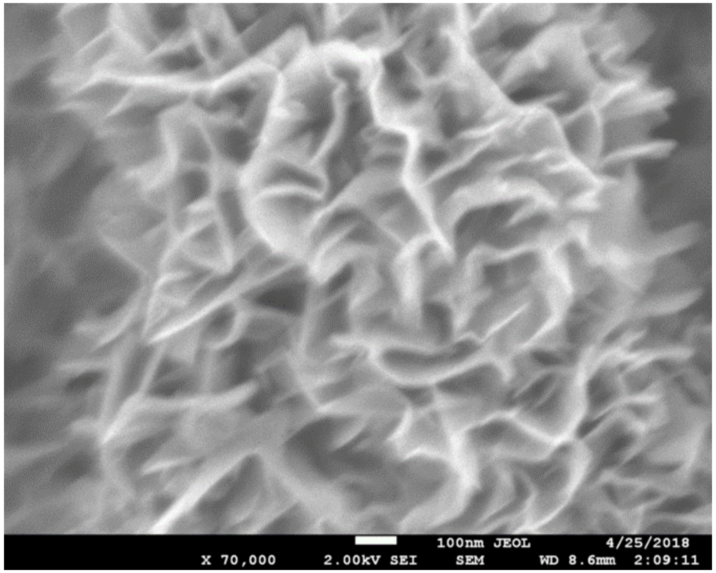
Advanced Capability via Graphene

Extremely black surfaces are created on the basis of graphene.

Exceeds the theoretical capability of conventional polymeric black surfaces, but also poses additional technical difficulties:



In situ growth as well as electrostatic deposition are both being trialed.

High-energy plasma discharge is required to access the more energetic regime needed for graphene synthesis.

Uniformity, reproducibility and quality are key.

Optical Extinction

Optical Extinction may occur via photon absorption, or by scattering (Rayleigh or other interactions).

Photons have the probabilistic ability to participate in transitions involving energy levels in a solid.

These energy transitions result in modifying the propagation velocity of light, resulting in an index of refraction, which in turn creates the possibility of light interactions with matter.

If energy transitions are not possible, the medium is perfectly transparent.

Scattering of Optical Photons

As a practical example, why is diamond transparent, but graphite is gray and disordered carbon is black, yet all three are carbon?	Carbon has low mobility but many charge carriers than can interact with passing photons, so it is black.
Metal reflects because it has free electrons. Graphite, as a semi-metal has few charge carriers but high mobility. It is black to silvery.	Diamond has high bandgap and almost zero charge carriers. Hence it is transparent.

Scattering of Optical Photons

Carbon can range from transparent diamond, to graphene, which may prove to the highest absorptivity material known.

Doped Few-Layer Graphene (very high carrier density & absorptivity).

↑

Surface Treated Nano (high extinction, 99+% absorptive)

↑

Highly Ordered Nano (high extinction, reflective/refractive)

↑

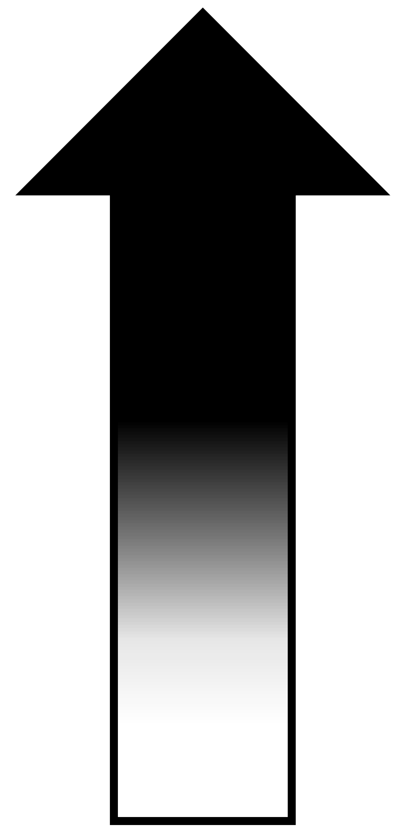
Highly Ordered Graphite (silvery gray semimetallic)

↑

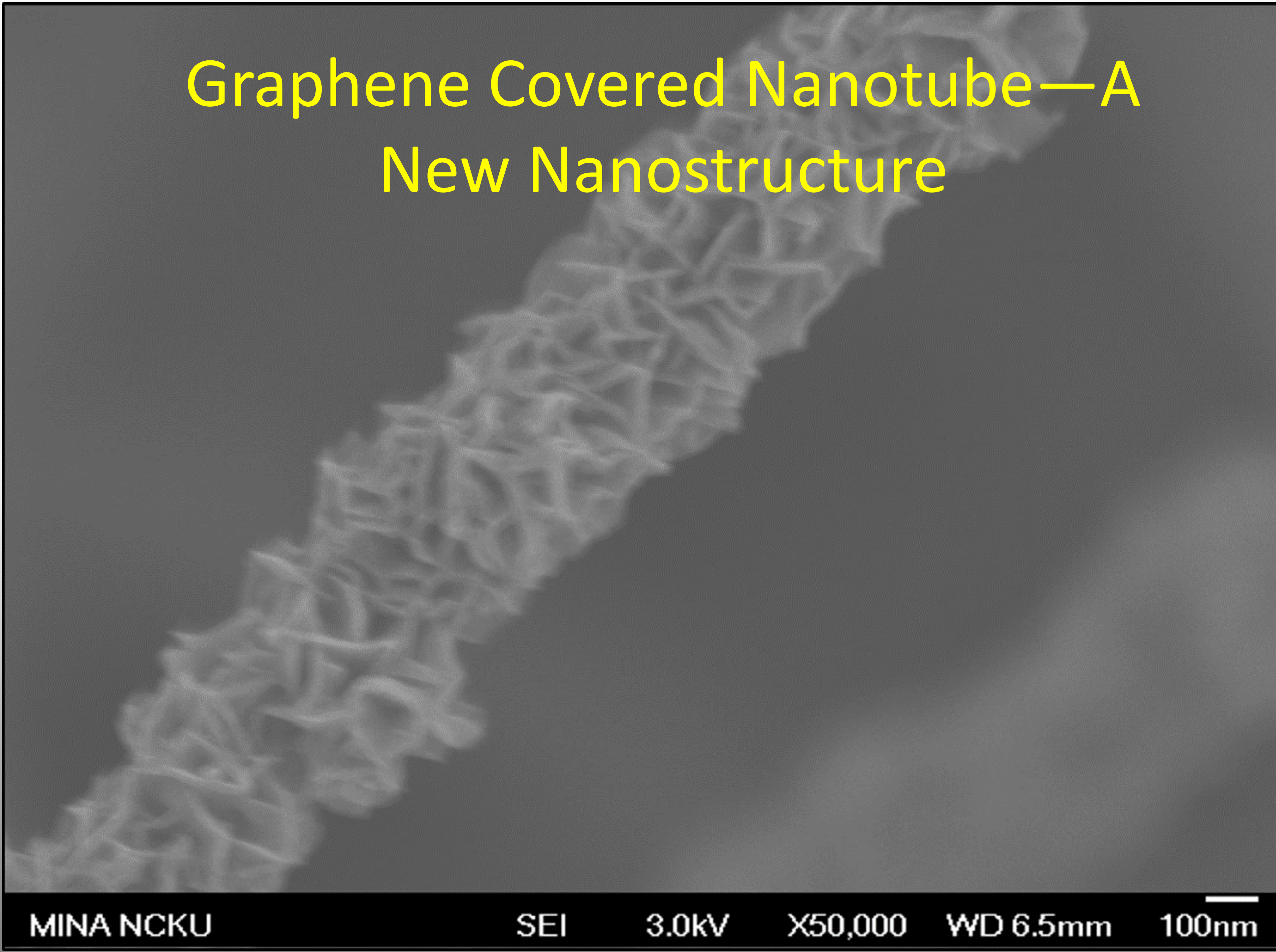
Doped Diamond, low mobility , low carrier density, translucent

↑

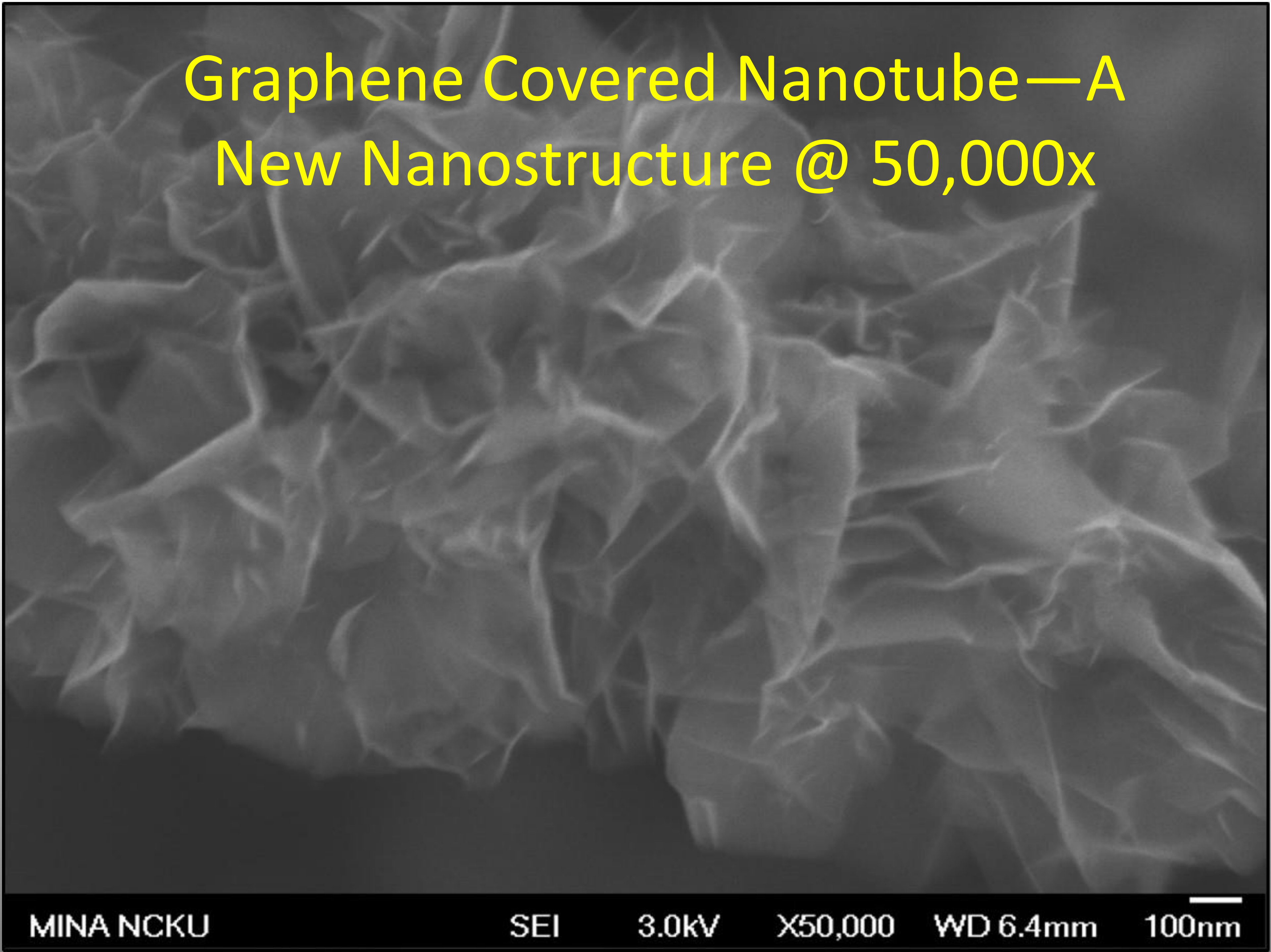
Diamond: Low mobility, near zero carrier density, transparent



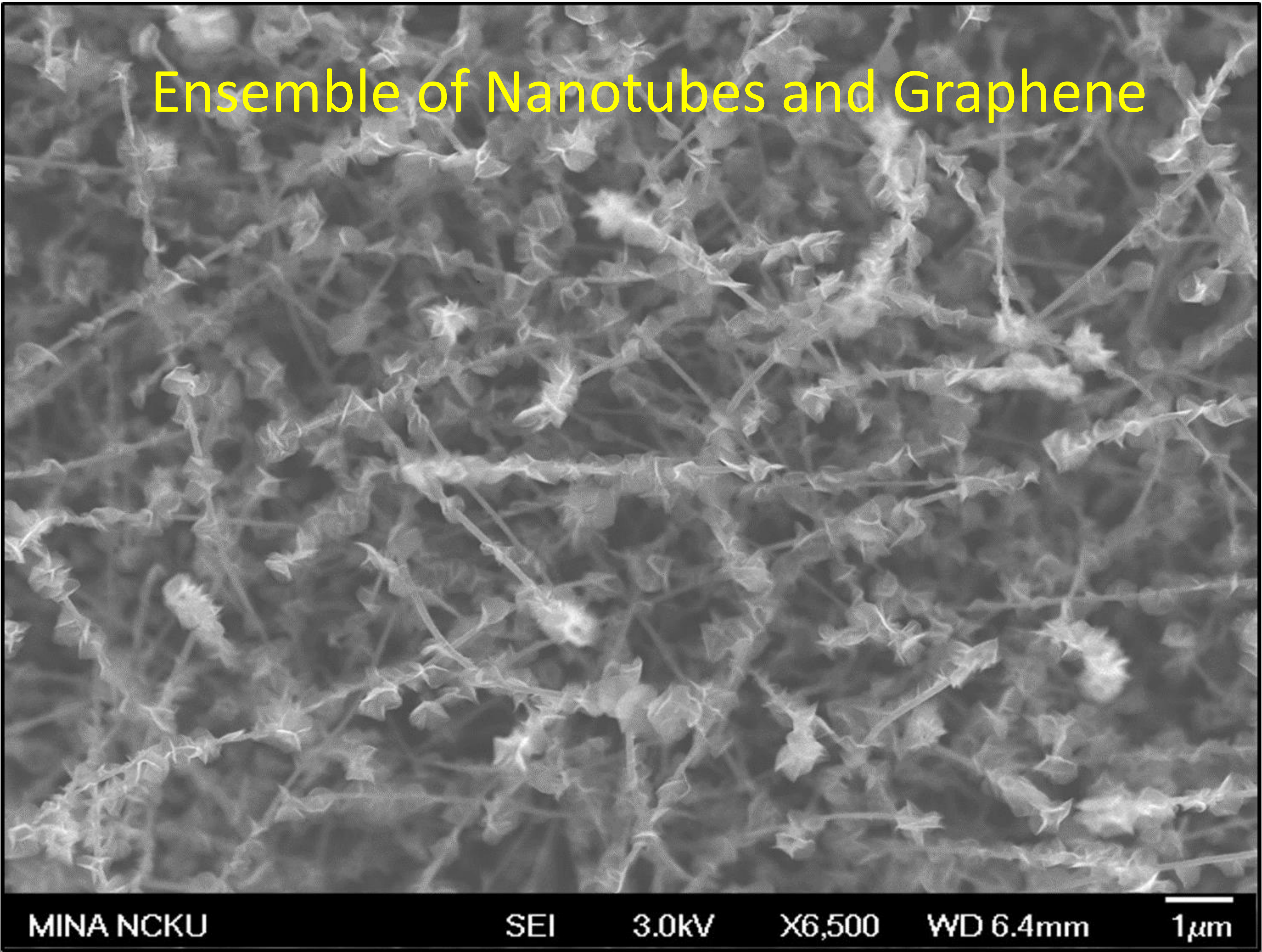
Graphene Covered Nanotube—A New Nanostructure

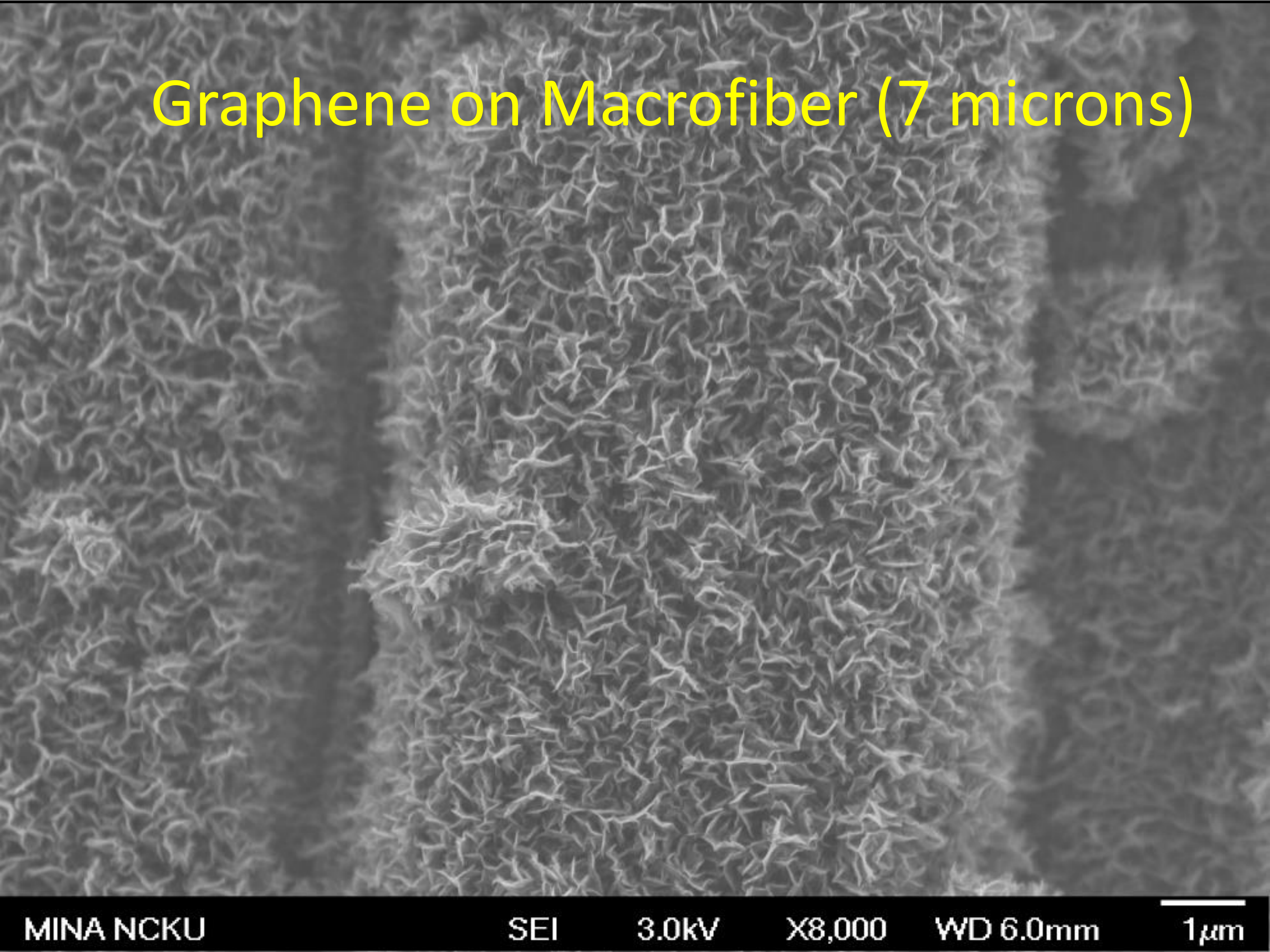


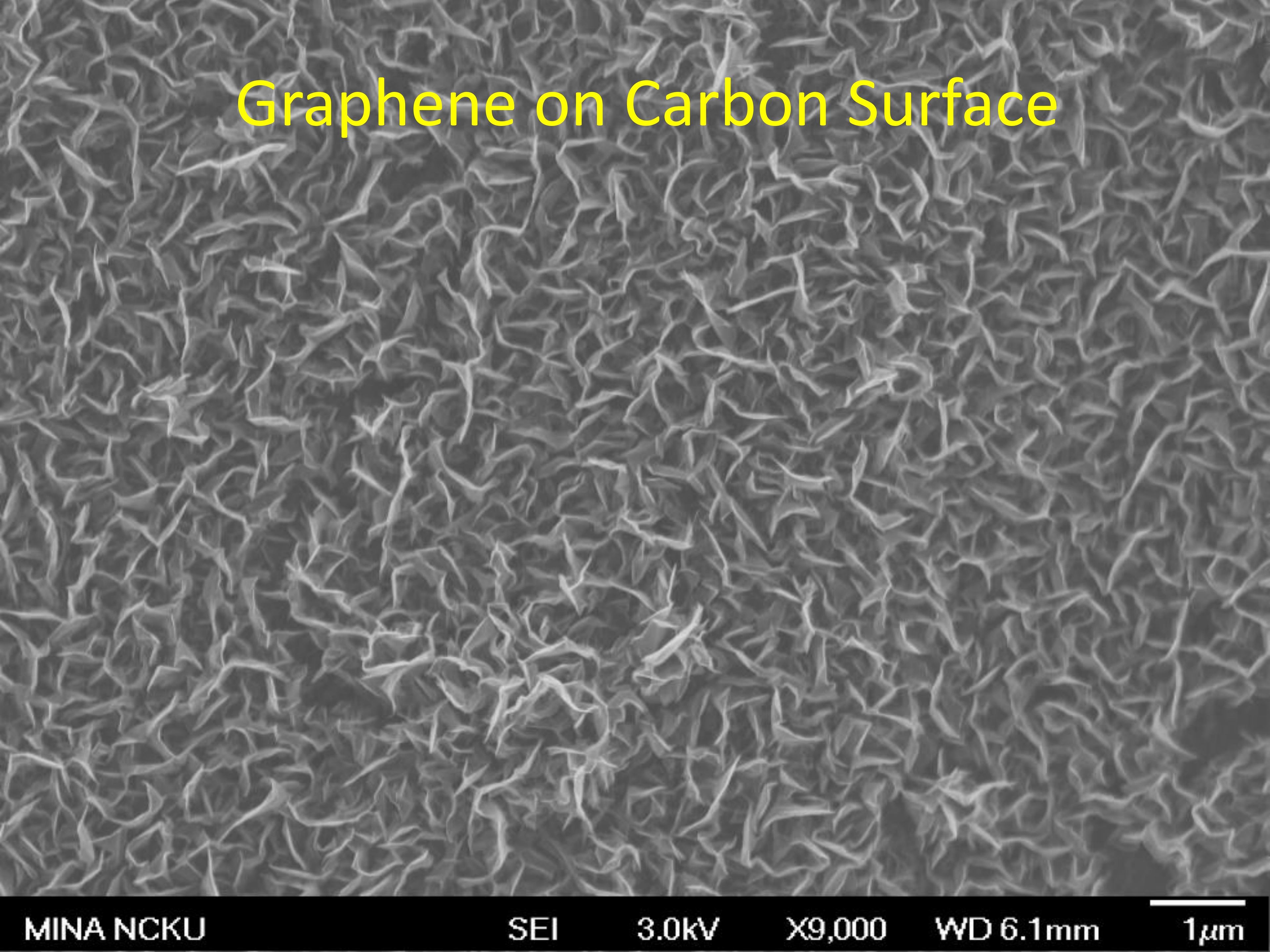
Graphene Covered Nanotube—A New Nanostructure @ 50,000x



Ensemble of Nanotubes and Graphene




Graphene on Macrofiber (7 microns)
MINA NCKU
SEI
3.0kV
X8,000
WD 6.0mm
1μm


Graphene on Carbon Surface
MINA NCKU
SEI
3.0kV
X9,000
WD 6.1mm
1μm

Determining the Number of Graphene Layers

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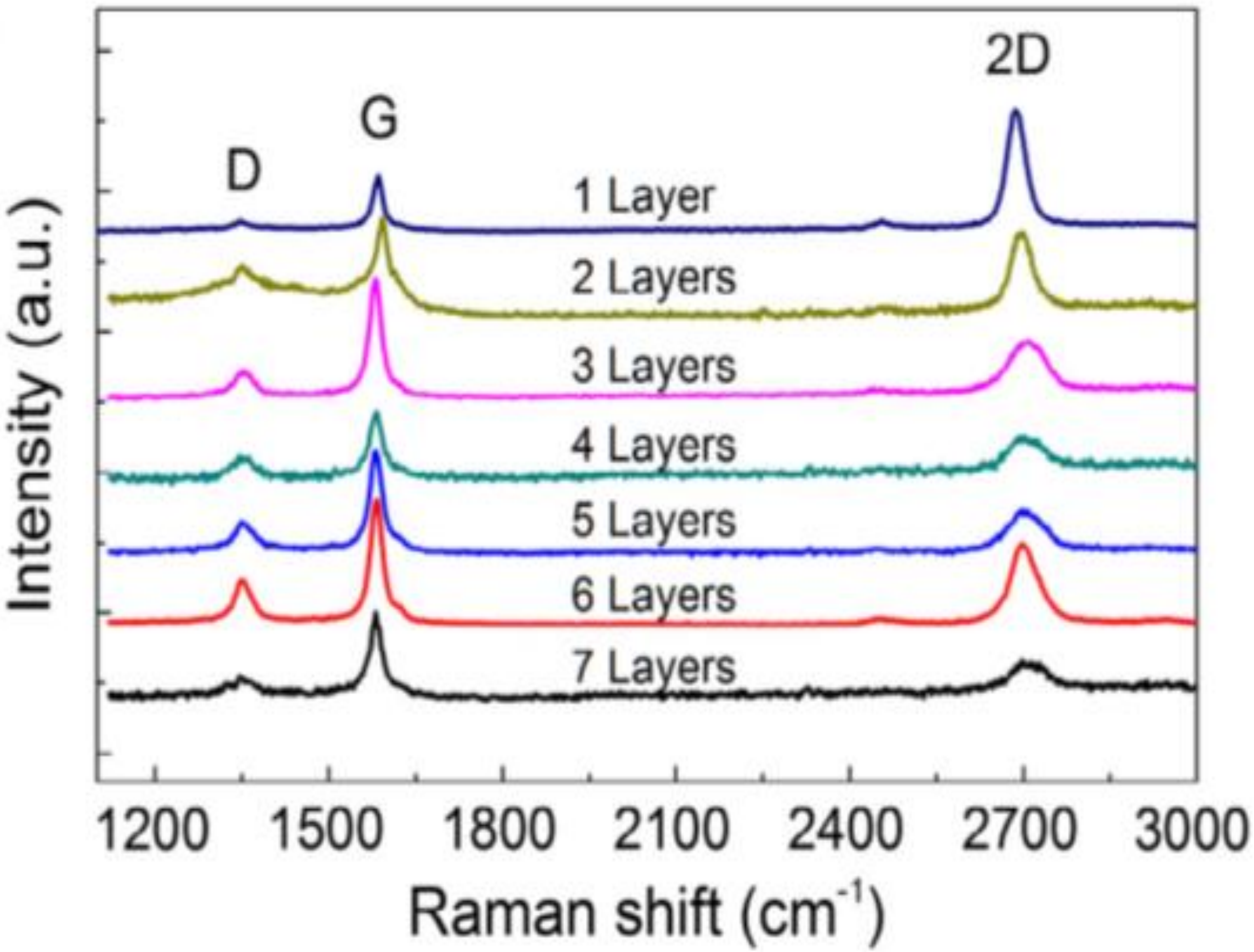

Determining the Number of Graphene Layers

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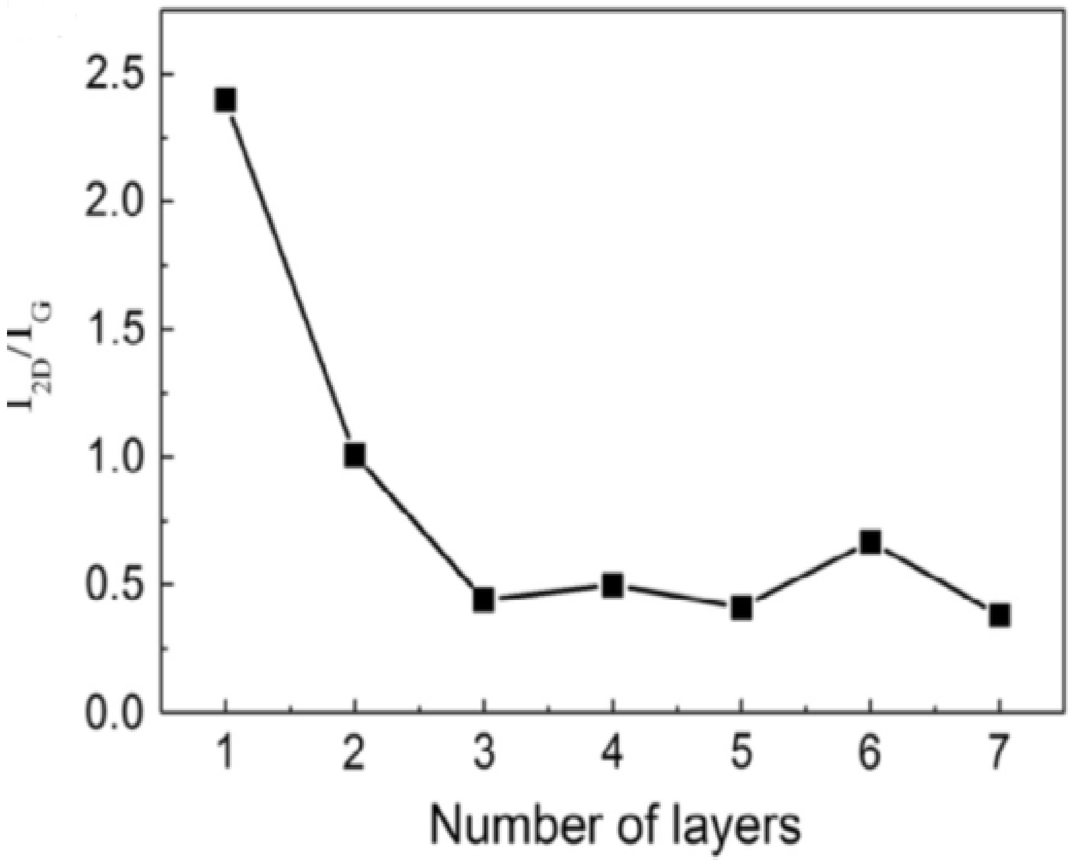
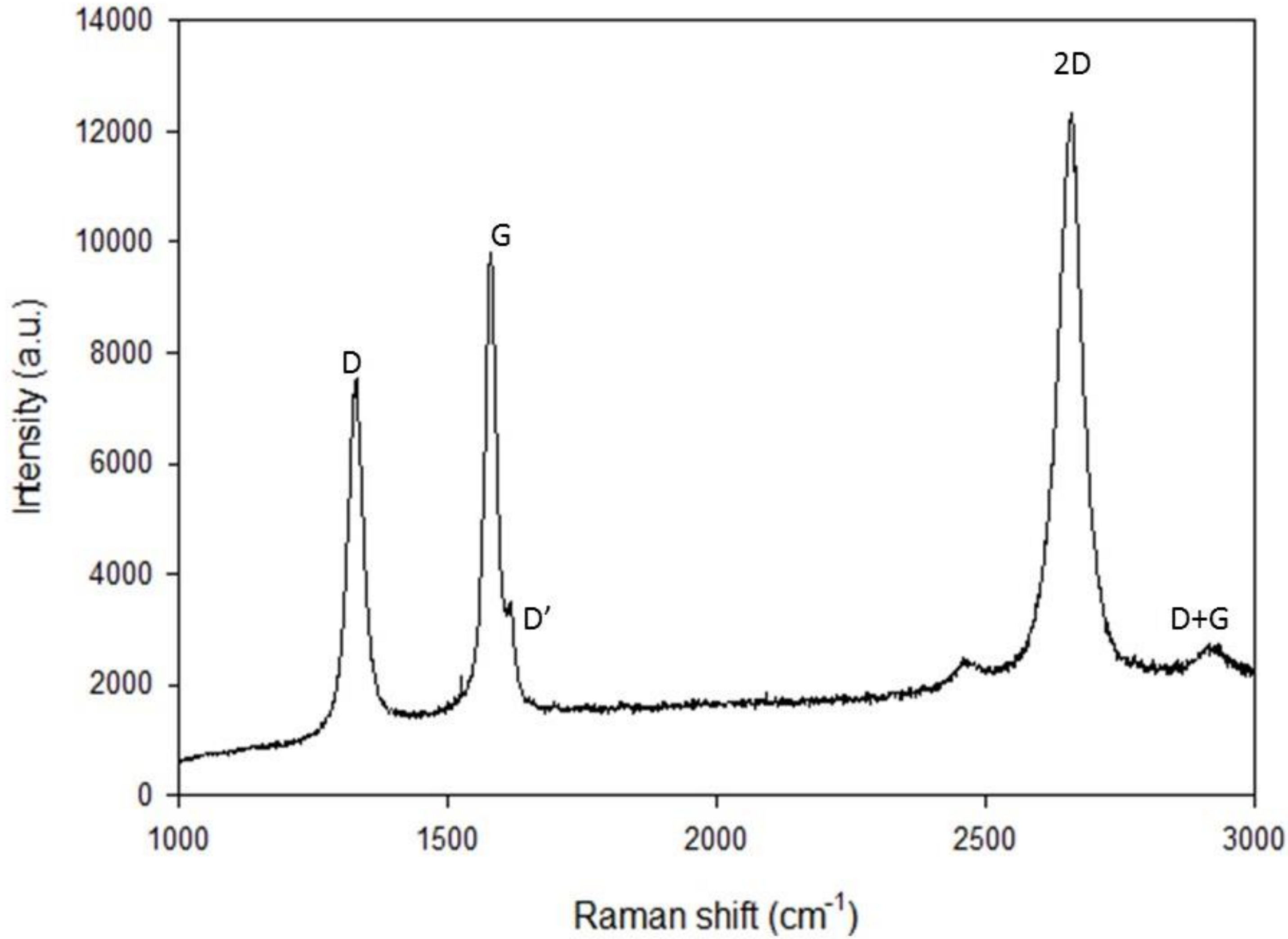


Tu et al.

Raman



14000
12000
10000
8000
6000
4000
2000
0
Intensity (a.u.)
1000
1500
2000
2500
3000
Raman shift (cm-1)
D
G
D′
2D
D+G

Working through the kinks

Reproducible manufacture of consistent dense graphene over 100% of a surface (substrate grown).

Reproducible manufacture of harvestable graphene for electrostatic deposition in a consistently dense application.

Quantity is limited currently to grams.

Discussion and Questions

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www.pyrografproducts.com
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Multi-scale image analysis (MSIA)

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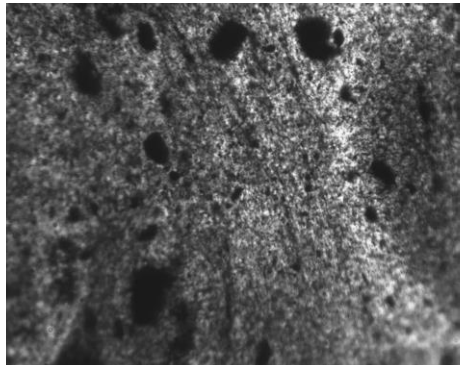
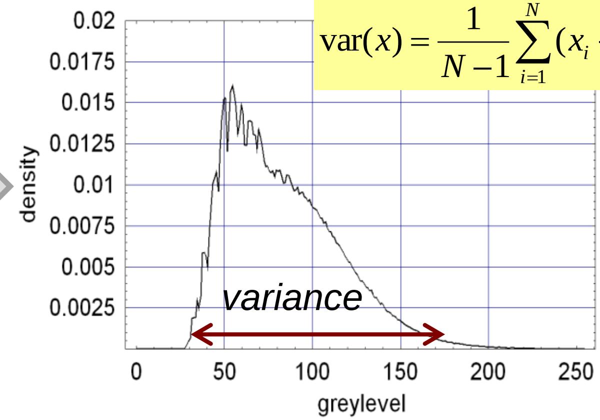
METHOD

Apply thin coating or solution on a slide





$$\mathrm{var}(x) = \frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2$$

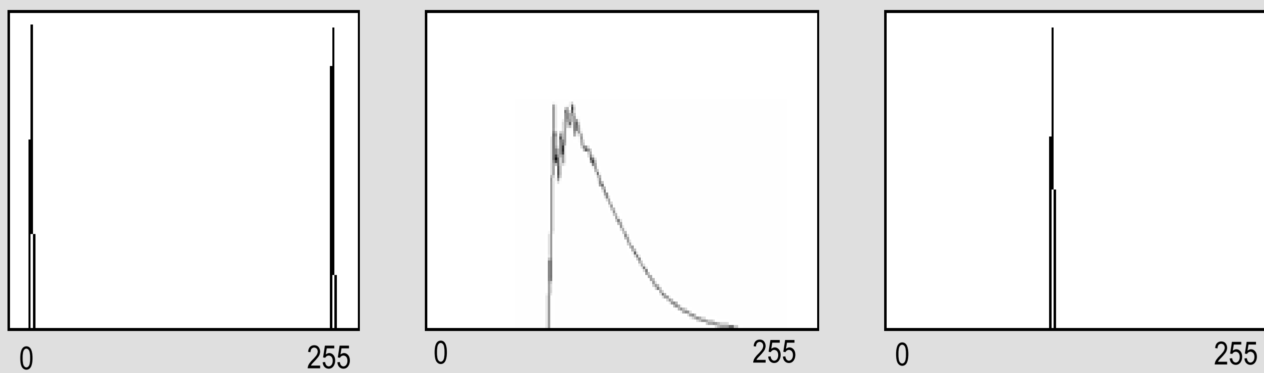
100 Optical micrographs

Dispersion analysis

- Optical micrographs
- Grey-scale histograms
- Variance

Decrease in resolution

The shape of the grey-scale histogram is directly related to the quality of the dispersion



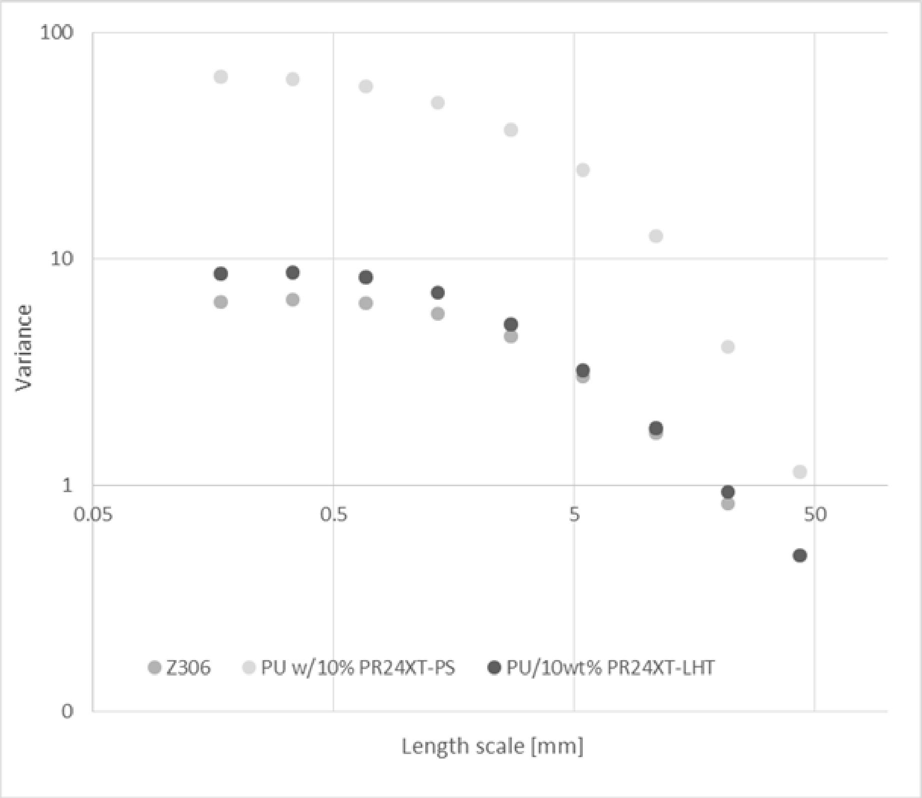
'No' dispersion | **Intermediate dispersion** | **'Perfect' dispersion**

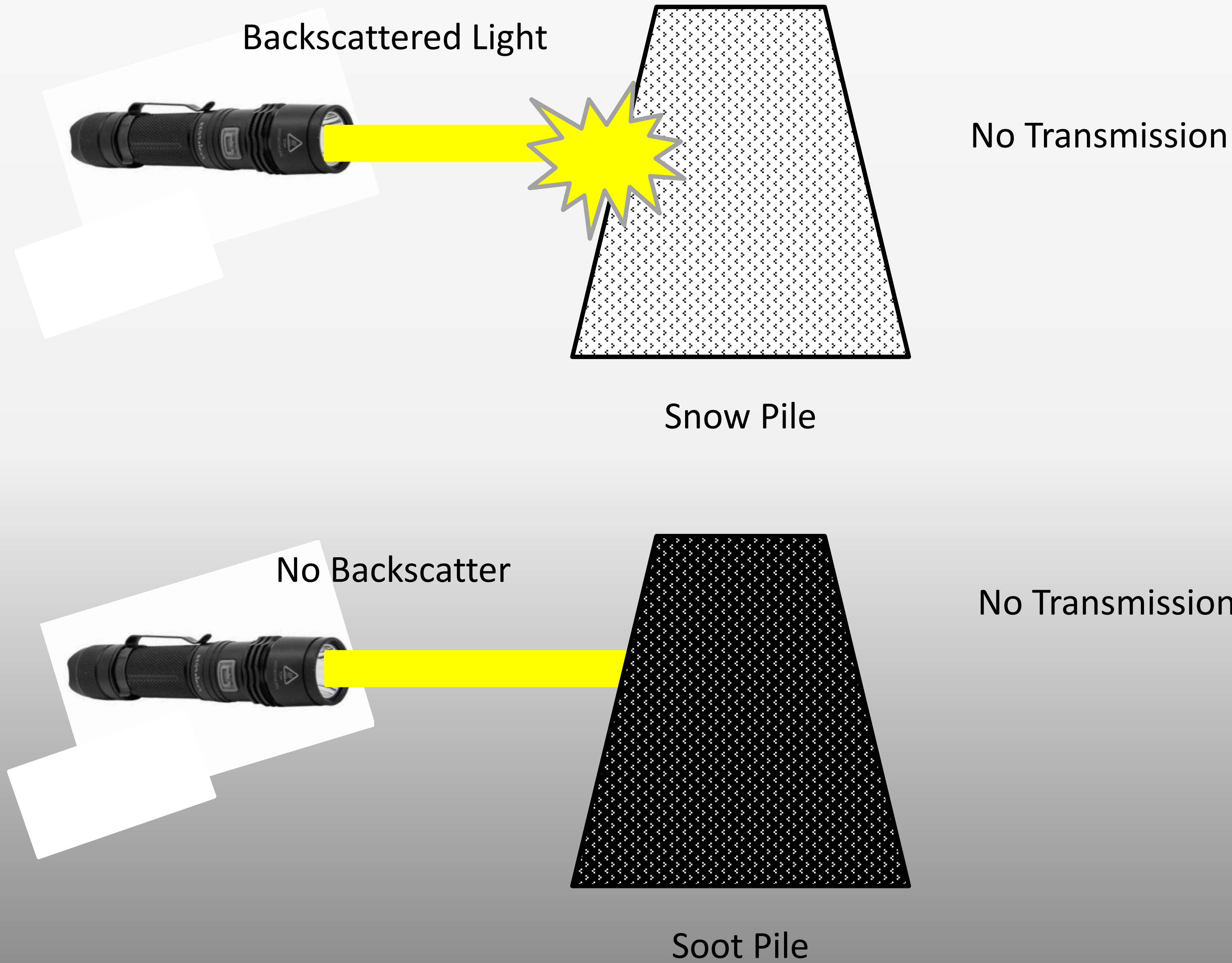
Van Hattum et al. SAMPE 2006 Fall Technical Conference, Dallas, USA, 2006.
Spowart et al., Materials Science and Engineering, A307, 51 (2001).

MSIA of Z306 and Z306 w/ CNF

PR24XT-LHT (dark grey) has a better dispersion in the Z306 than the PR24XT-PS (light grey), and is close to the Z306

The dispersion analysis results allow us the establishment of relationships and draw more tangible conclusions, once related to the reflectivity and flexibility properties of the coatings




Backscattered Light
No Transmission
Snow Pile
No Backscatter
No Transmission
Soot Pile