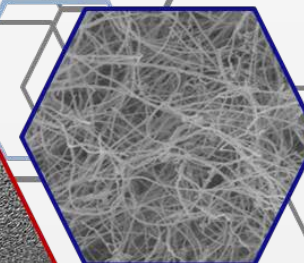
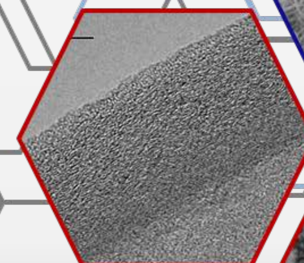
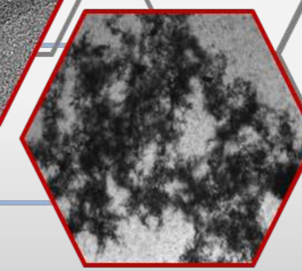
Pyramid Nanostructured Coatings for Stray Light Suppression







Mirror Technology SBIR/STTR Workshop 2017 |Nov 14-17, 2017|

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Applied Sciences Inc
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Cedarville, Ohio

Overview

- Company Background
  - Carbon Nanofibers
  - Polymeric Coatings
- Problem Statement
- Program Goals
- Approach
- Results
- Discussion

Company Chronology

- **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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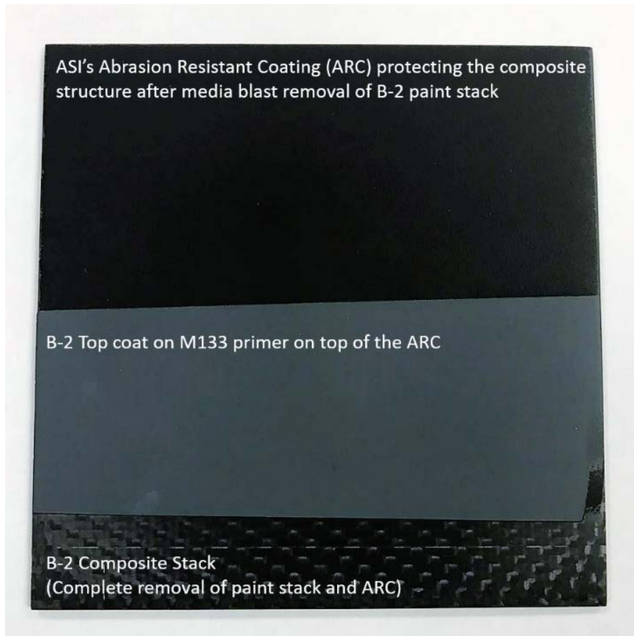
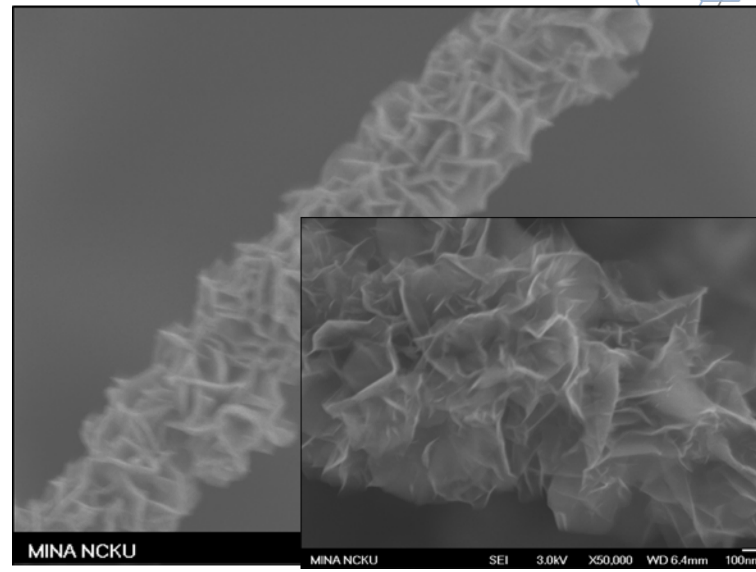
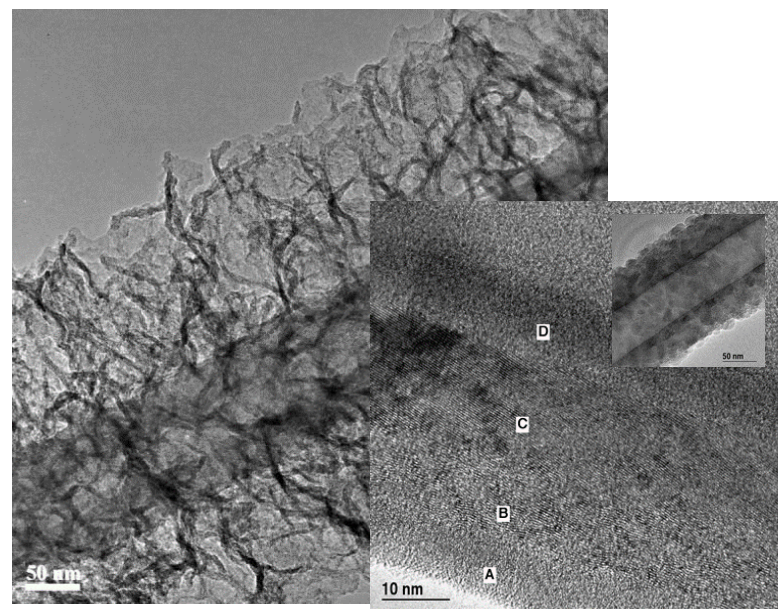
R&D of novel carbon forms and vertical integration







Pyrograf Products, Inc

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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

Carbon Nanofibers

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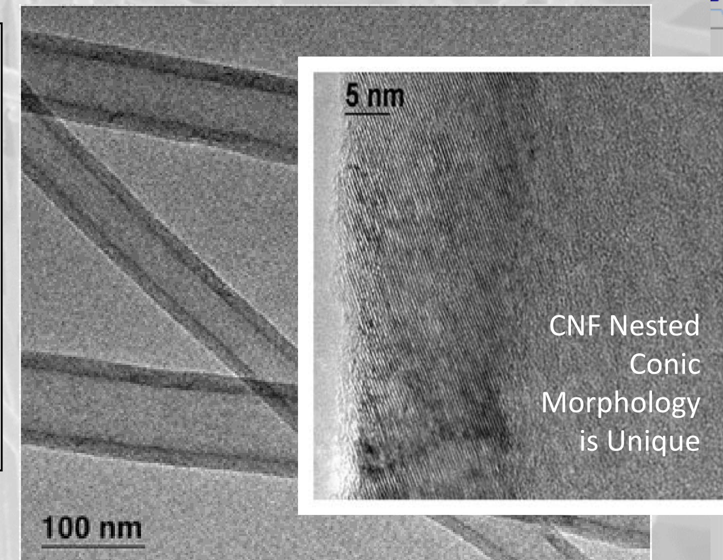
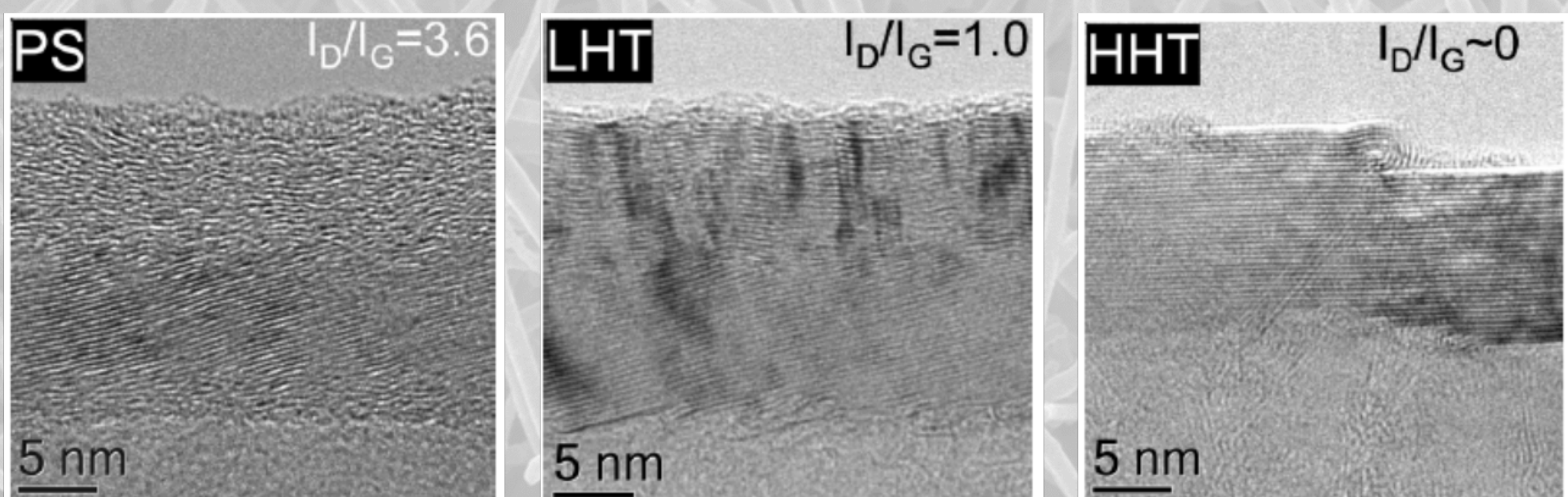
Carbon Nanofibers (CNF)

- *Trade name:* Pyrograf-III.
- *Diameter:* ~ 50-200 nanometers
- Provides electrical, structural, and thermal/ ablative properties.
- *Current status:* Pilot scale production, intermediate cost.
- *Uses:* Conductive polymers, EMI shielding, structural enhancement, abrasion resistance.
- *Potential market:* >1500 TpY



Annealing temperature > higher degree of graphitization > Electrical conductivity



HRTEM of CNF annealed at different temperatures as well as D/G ratio calculated from Raman spectra

CNF vs CNT

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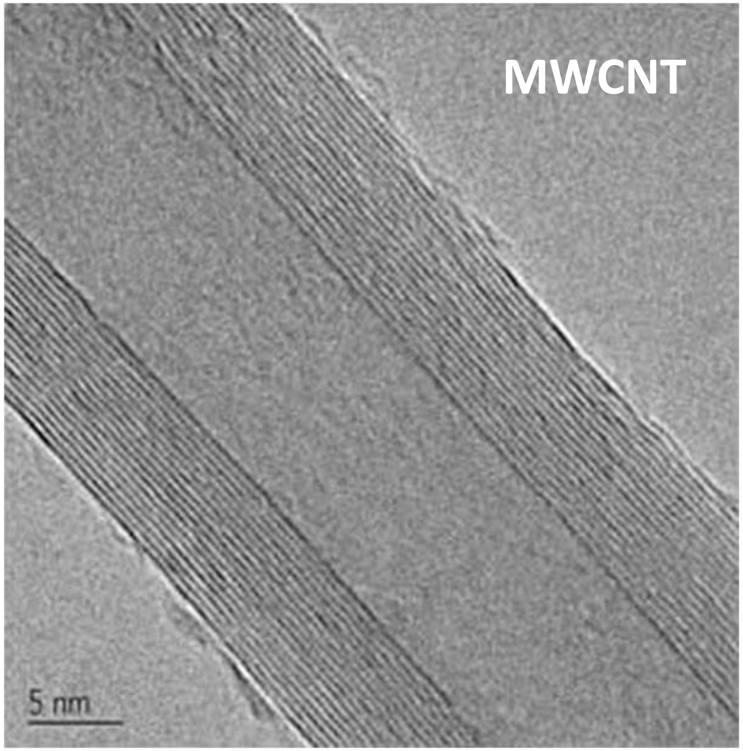

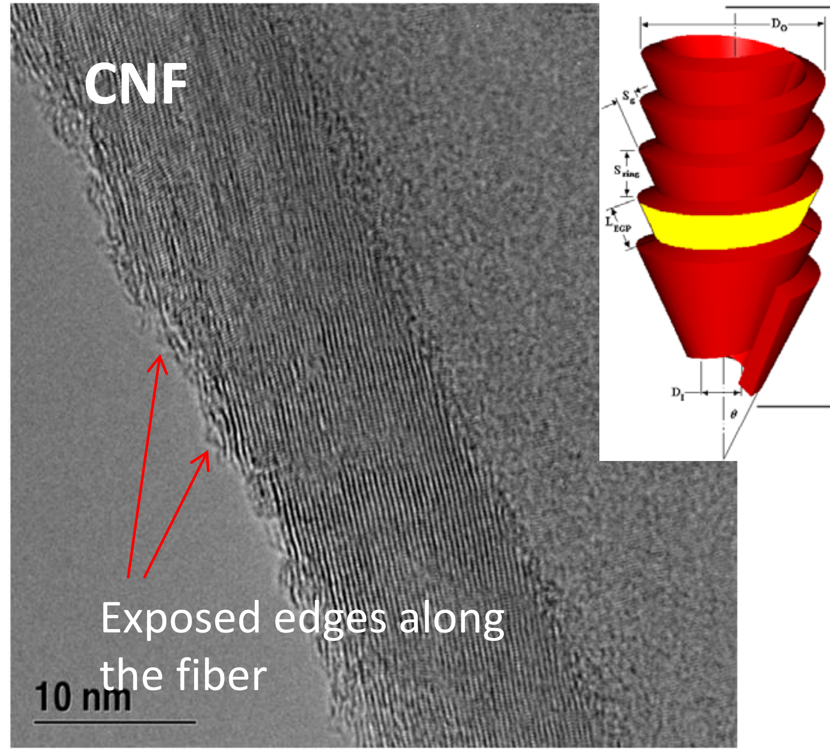

Benefits of using CNF over CNT

- ❑ Easier to disperse
- ❑ Easier to process
- ❑ Easier to functionalize
- ❑ Simultaneously provides electrical and mechanical property enhancements
- ❑ Lower overall cost of use

Advantages of Carbon Nanofibers

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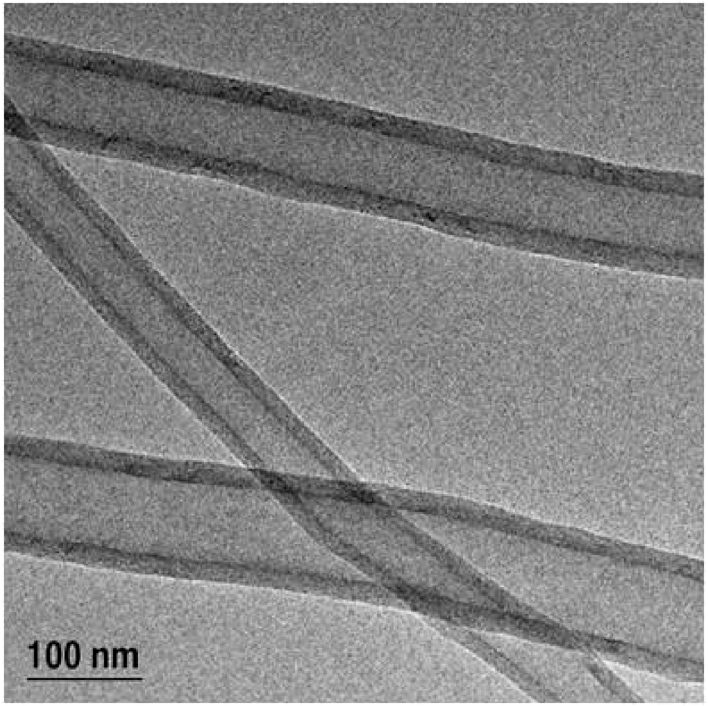
Functional and morphological merits of CNFs for polymeric applications:

- High aspect ratio (l/d) – 100 – 1000
- Thermal conductivity up to 5 x copper
- Electrical conductivity overlaps metals
- Multi-functionality
- Easier to disperse than CNTs[1]
- Higher chemical reactivity
- Recyclability
- Available in high volumes at a competitive price
- High quality



[1] M.Nyden,Polymer, 49: p. 635, (2008).

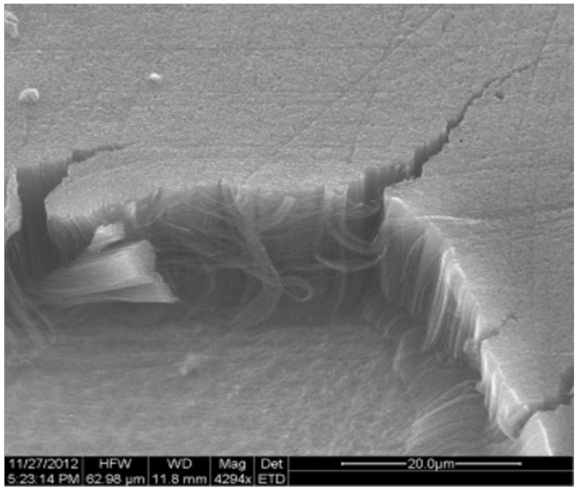
Problem Statement

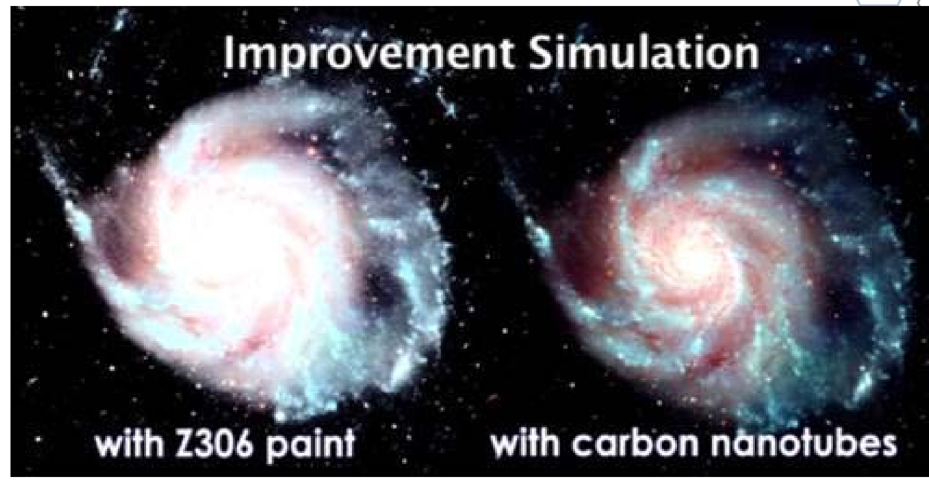
Up to 40% of images taken of earth's surface are rendered unusable due to stray light contamination.

Stray light caused by scattering on optical surfaces degrades the spatial resolution of observations.

To improve image quality and usage rate of astrophysical images taken via telescopes, it is necessary to minimize the amount of stray light that can be reflected.

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 I Goals:

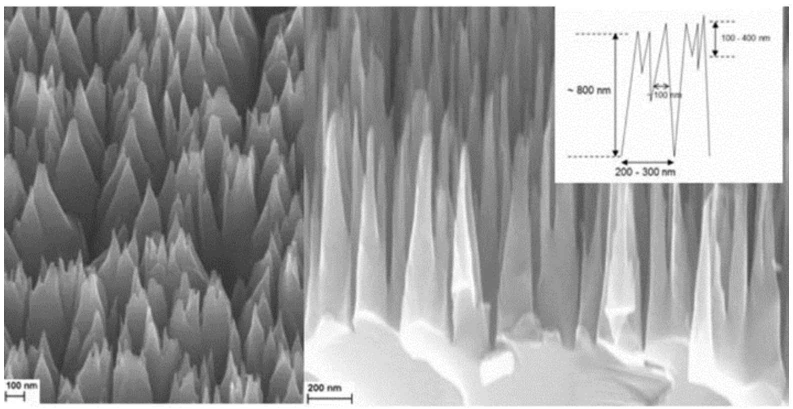
NASA is seeking new coating technologies based on carbon nanotubes that can achieve a broadband reflectivity of less than 0.1%, have good adhesion to protective metal coatings and with superior mechanical properties to withstand launch conditions.

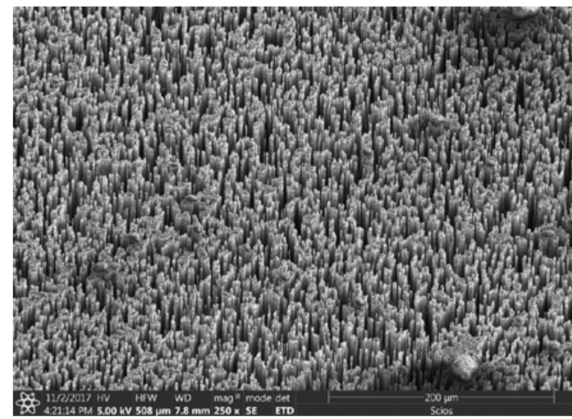
Applied Sciences, Inc. (ASI) proposes to develop a nanostructured non-reflective surface coating that will effectively regulate and control broadband reflectivity to a capacity of less than 0.1%.

- *The proposed effort is to develop and validate a **combined materials** and **manufacturing approach** that will couple tailoring of an aerospace qualified polyurethane resin, like the Z306, using stacked-cup carbon nanotubes with a unique manufacturing approach that will produce a pyramid nanostructured surface.*
- *This new approach comes at a **much lower cost**, is **readily scalable** and **safer** than the current technology*

Approach:

Develop a unique solution for stray light suppression, which utilizes nano-structured polymer coatings combined with a proven and scalable processing method that will yield a nano-textured surface.





Make use stacked-cup carbon nanotubes in the legacy polymer system, which will provide additional absorptive properties.

Use plasma etching to fabricate black silicon nanostructures capable of suppressing light by 99%

Use polymer replication techniques to impart the black silicon light suppressing structure onto the CNF developed black coating

PDMS-stamp into pyramidal nanostructures for broadband absorption with efficiency at or better than 99.9%

Deep Reactive Ion Etching

DRIE Fabrication of Black Silicon :

One-step maskless deep reactive ion etching (DRIE), that produces high aspect-ratio micro structures, also known as Black Silicon (BS) on a single crystal silicon wafer under cryogenic temperatures;

BS is obtained in a plasma compound of SF_6 and O_2 under controlled process conditions.

$$Si + xF^* \rightarrow SiF_x$$

$$SiF_x + yO^* \rightarrow SiO_yF_x$$

The geometry, density, height and width of the nano-structures can be manipulated by changing the etching conditions;

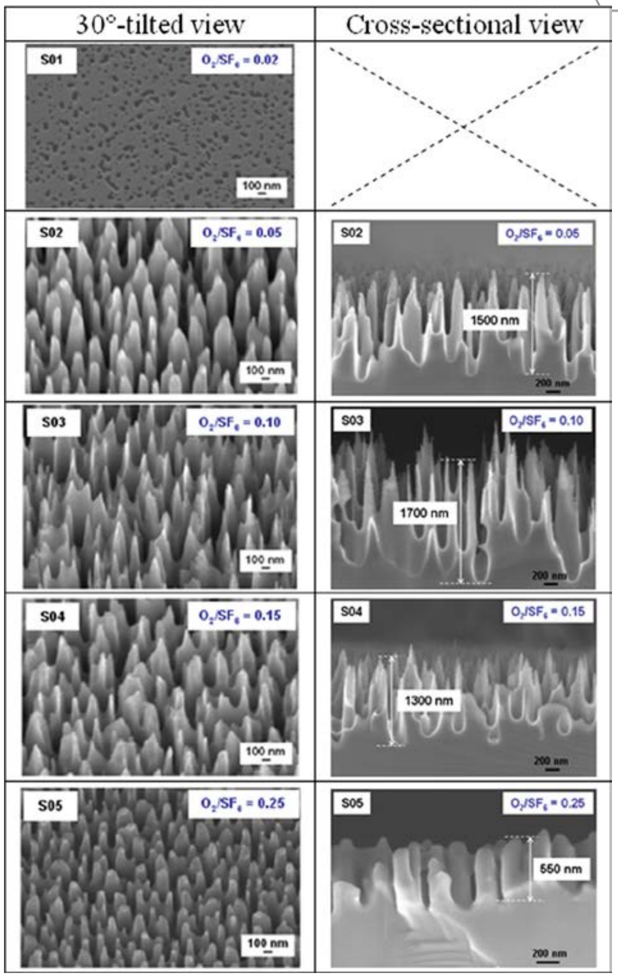
Variable Parameters:

O_2 Flow rate; Etching temperature; Temperature of the silicon wafer and bias voltage.

Fixed Parameters:

ICP power, gas pressure and SF_6 gas flow rate.

High throughput process;



SEM images with 30˚-tilted and cross-sectional view of samples with different ratios O2/SF6.[1]

1-Nguyen, et al. J. Appl. Phys. 113, 194903 (2013); doi: 10.1063/1.4805024
2- Nguyen et al. *Black Silicon with Sub-Percent reflectivity: Influence of the 3D Texturized Geometry, June 2011*.

Polymer Replication

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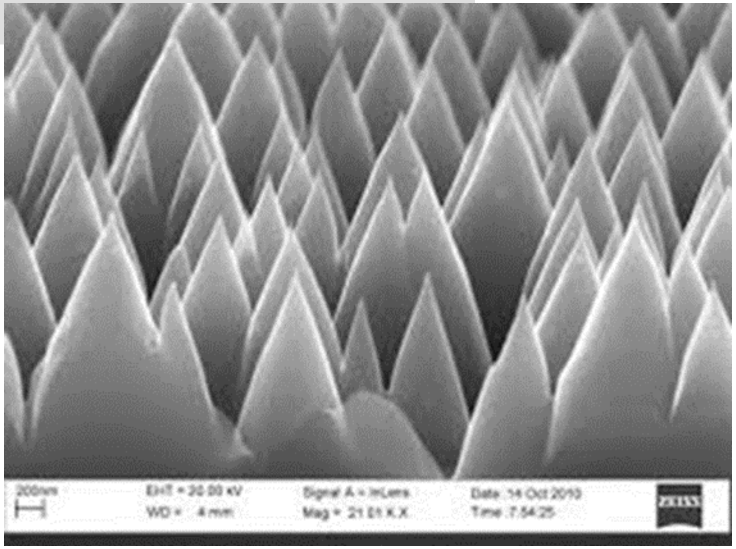
Making use of BS structures as a template for polymeric coatings



- Sainiemi et al.[3] showed that the densest arrays of nanospikes with slightly positively tapered sidewalls had the lowest optical reflectance, while pyramid-shaped nanospikes were ideal for use as templates for polymer replication.

- Polymer replication techniques have a high-throughput and are low-cost methods which make them very attractive for this application.

- An elastomeric stamp is produced by casting a PDMS layer on top of the structured silicon surface. The PDMS stamp is thermally cured and peeled off.

- PDMS stamp serves as template for the anti-reflective coating

Sainiemi, L. et al. Adv. Mater. 2011, 23, 112-126. DOI:10.1002/adma.2010018100

Why use a Polymer Coating?

- 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;

CNF Coating Development

Applied Sciences, Inc.

Chemglaze Z306 Spacecraft Heritage*

MSX Spirit III Telescope Baffles
EO-1 Land Imagers Housing
UARS CLAES
Hubble Telescope
Mars 96 PFS LW Channel Housing
GOES Imager Sounder Telescope Baffles
POES AVHRR/3, HIRS/3 Telescope Baffles
LANDSAT Thematic Mapper
EOS-AM MODES
Small Explorer WIRE

Chemglaze Z306 is Spacecraft Qualified;
ASI CNF have been Spacecraft Qualified;
Very likely can be significantly improved.

**Z306 is produced and distributed by Socomore*

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. In this present application, the coating viscosity has to allow for stamping the nano-spikes and post-cure release of the PDMS stamp.

*MSIA was jointly developed by ASI and WPAF Research Labs

How can we monitor dispersion in nanocomposites?

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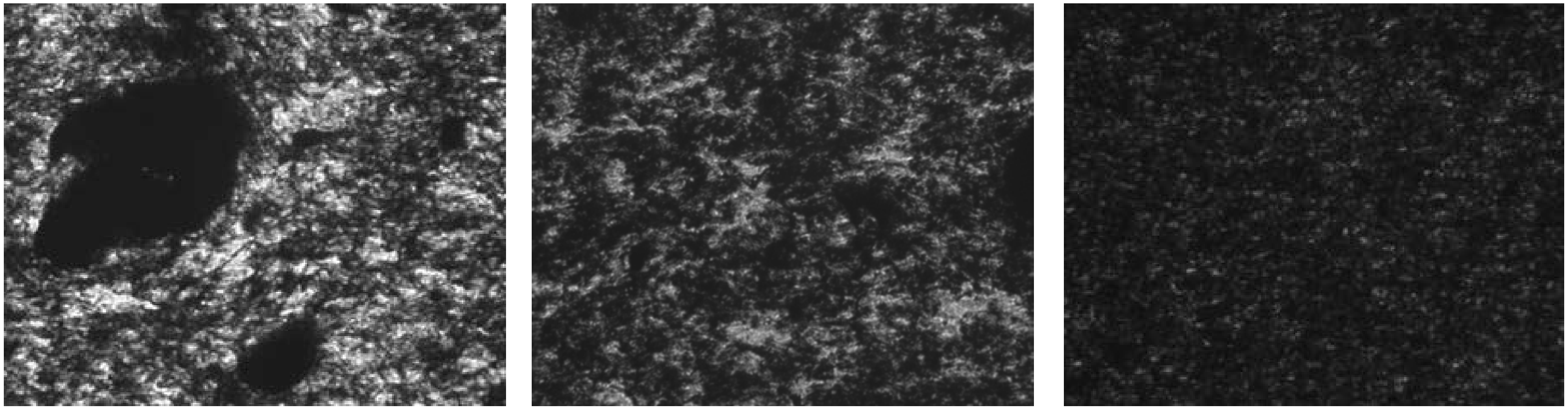
Same filler, same loading



HDPE/ 5wt%CNF Masterbatches

50 µm

3 different processing conditions

3 different dispersion levels

3 different composites

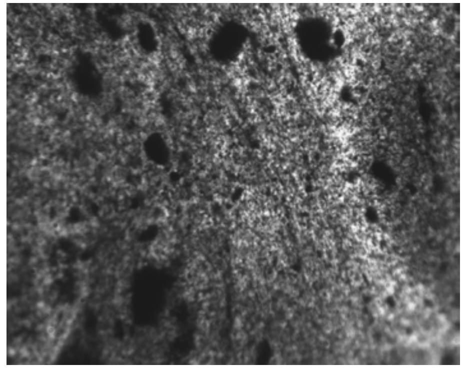
Most methods used for assessing fiber dispersion are **subjective**, **non-reproducible** and with a **limited sampling area**

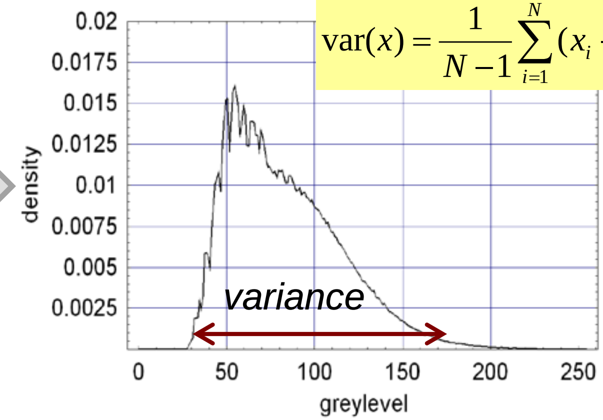
Multi-scale image analysis (MSIA)

Applied Sciences, Inc.

METHOD

Apply thin coating or solution on a slide





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

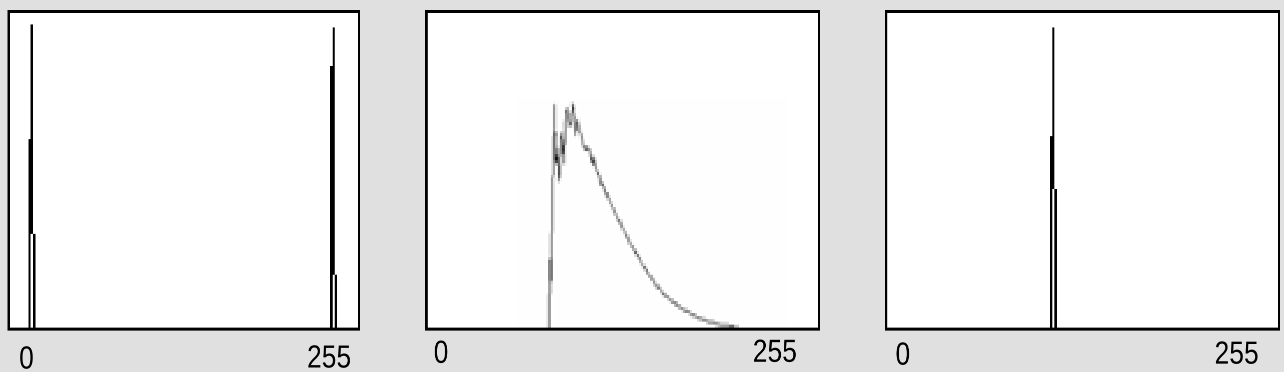
100 Optical micrographs

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).

Pyramid Nanostructured Coatings

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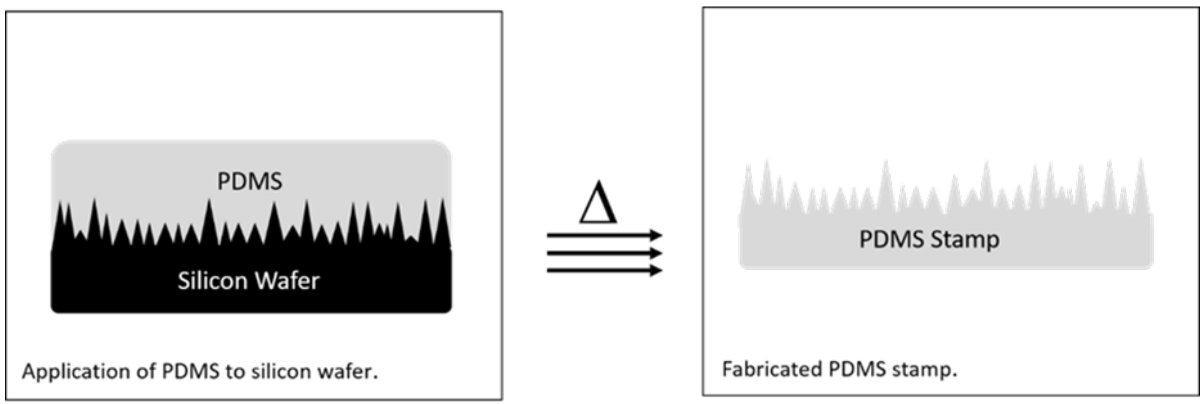
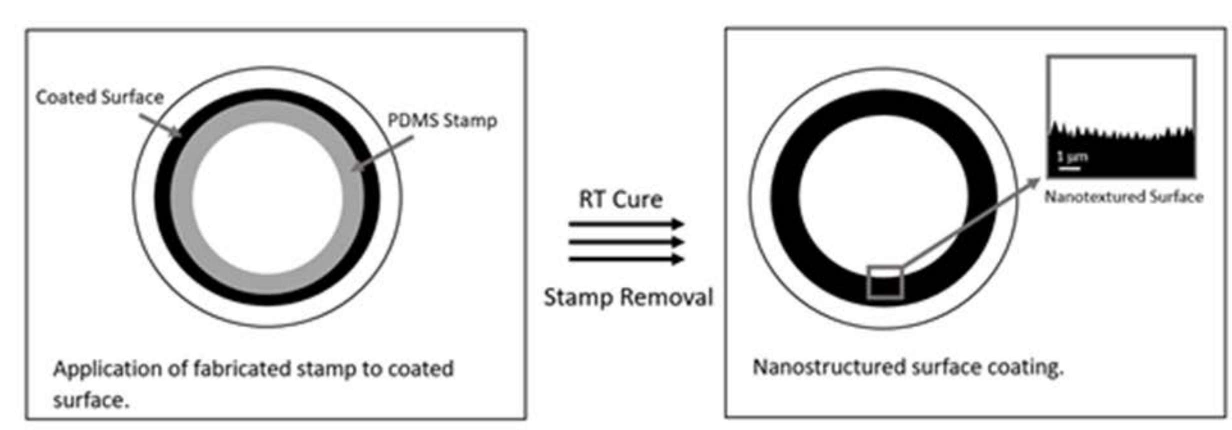
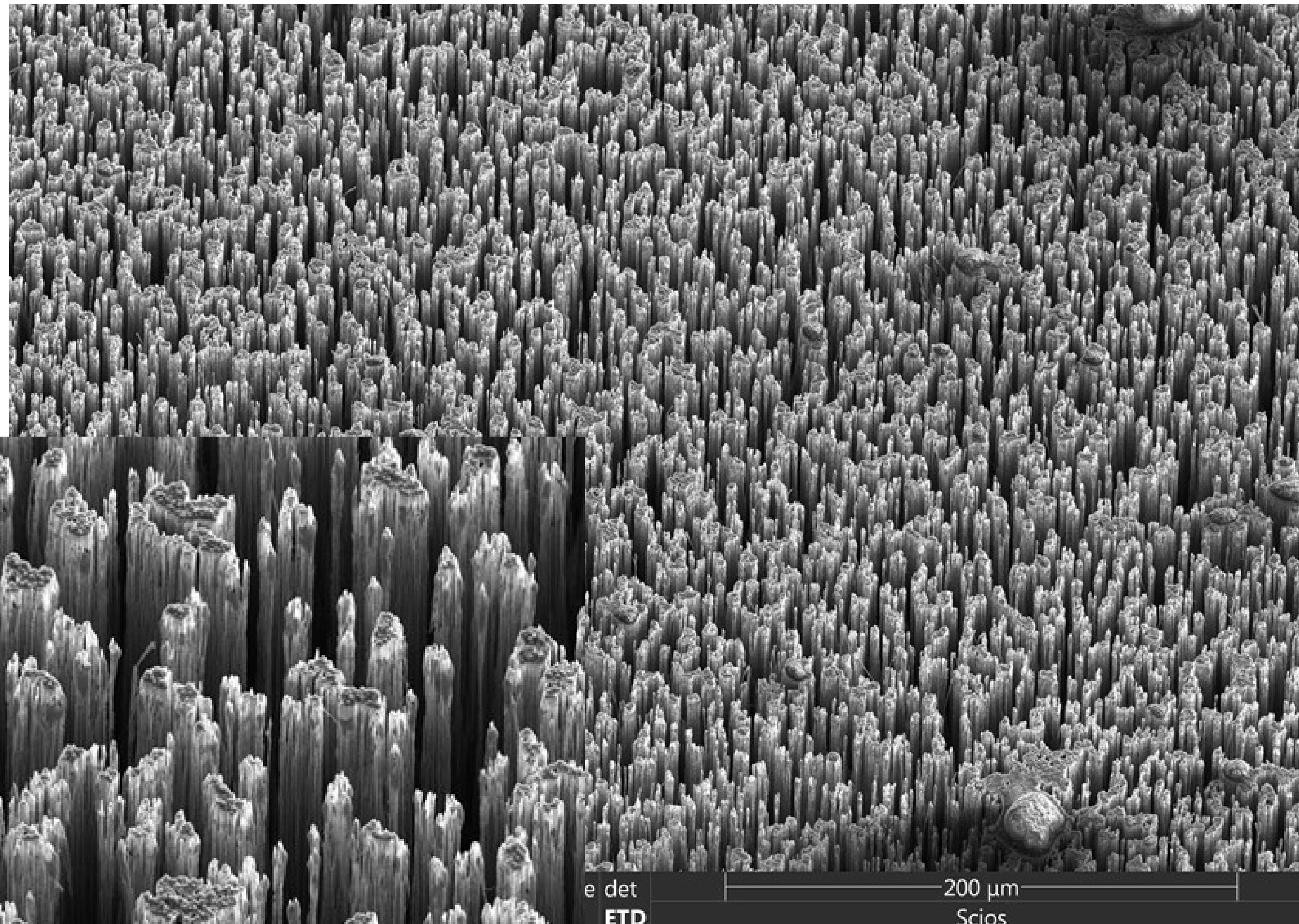
Stamp Fabrication

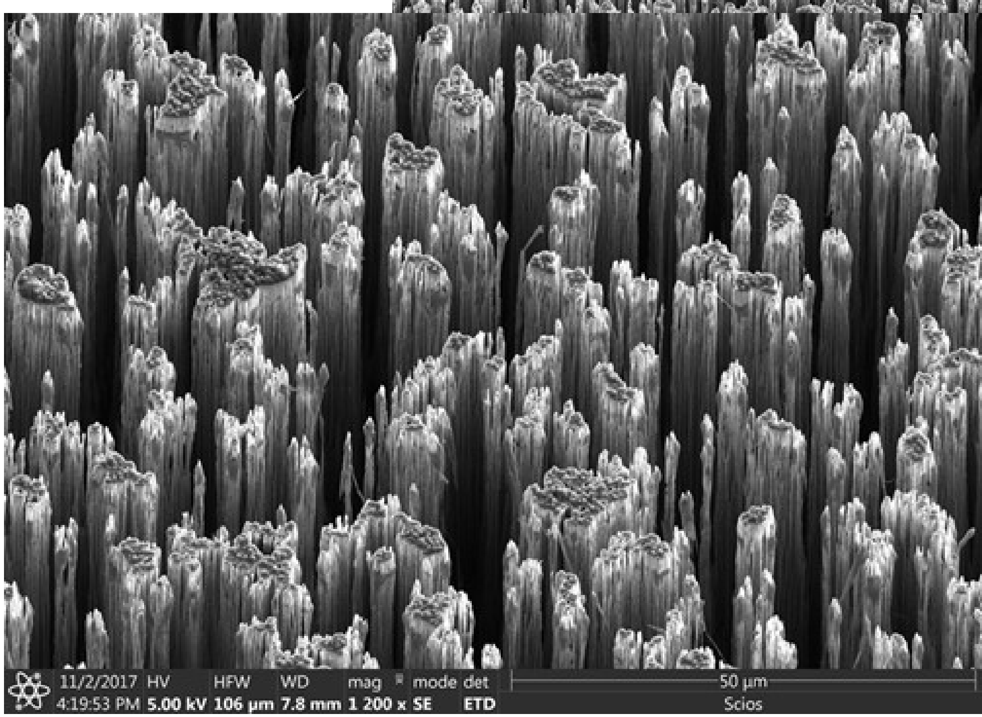


Nanotextured Surface Construction



PDMS Stamped Nanotextured "Forest"





Accomplishments

- Nanocoatings with Chemglaze Z306 fabricated and are currently being characterized.
- Joint Development/License Agreement signed with Socomore (producer of Chemglaze® products).
- Silicon wafer with high aspect ratio “nanotextured polyforest”
- ASI approach focused on already-space-qualified polymer.
- Technological enhancements possible with few-layer graphene sub-domain.

Coming next ….

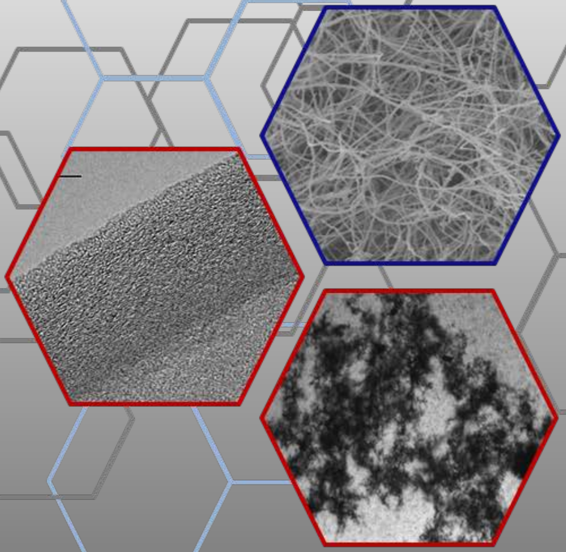
Determine if the developed nano-textured coating meets the specifications for scattered light suppression coatings:

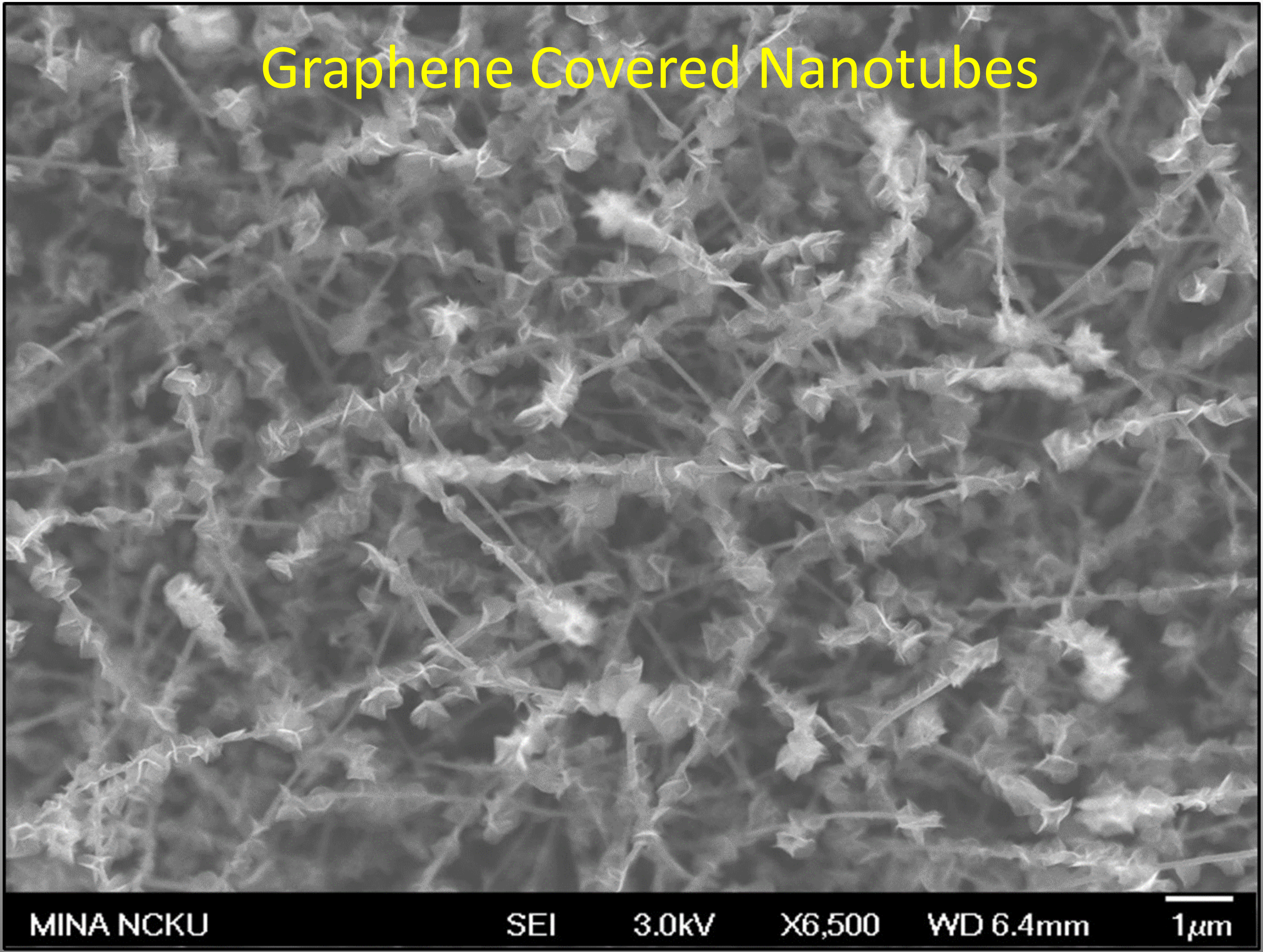
- ✓ broadband reflectivity of 0.1% or less: SEM/ hemispherical reflectance.
- ✓ withstand launch conditions: ASTM D552 Composite Flex Testing/ Hardness
- ✓ adhere to multi-layer dielectric or metal coating, including IBS coating: ASTM D4541 Pneumatic Adhesion Tensile Testing Instrument (PATTI)

NASA Spacecraft Launch Vibration and Environmental Standards

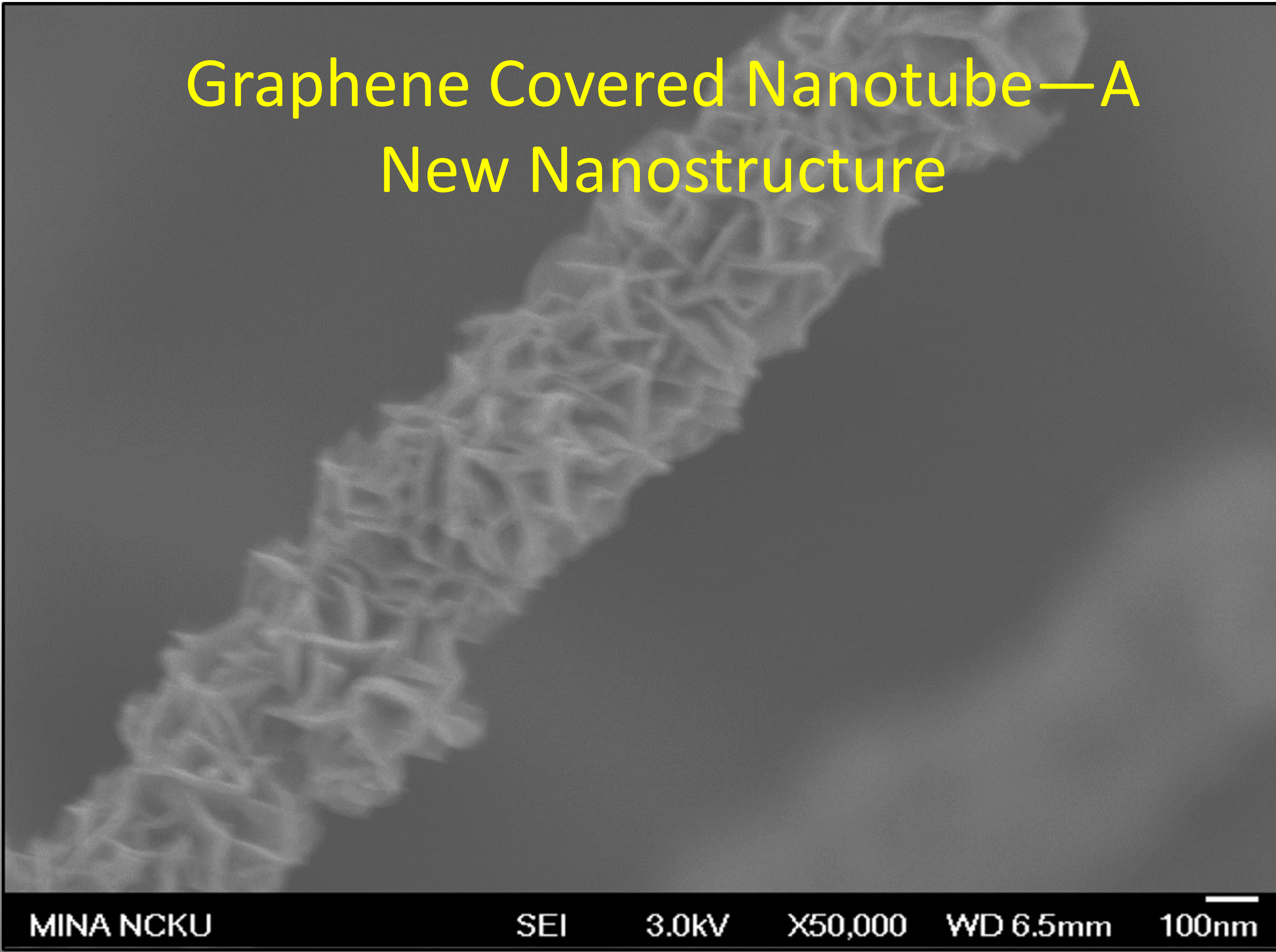
NASA-STD-7002 Payload Test Requirements
NASA Force Limited Vibration Testing
NASA-HDBK-7004
NASA-STD-7001 Payload Vibroacoustic Test Criteria
NASA Sine-Burst Load Test
NASA Acoustic Noise Requirement
NASA Combination Methods for Deriving Structural Loads

Graphene Covered Nanotubes

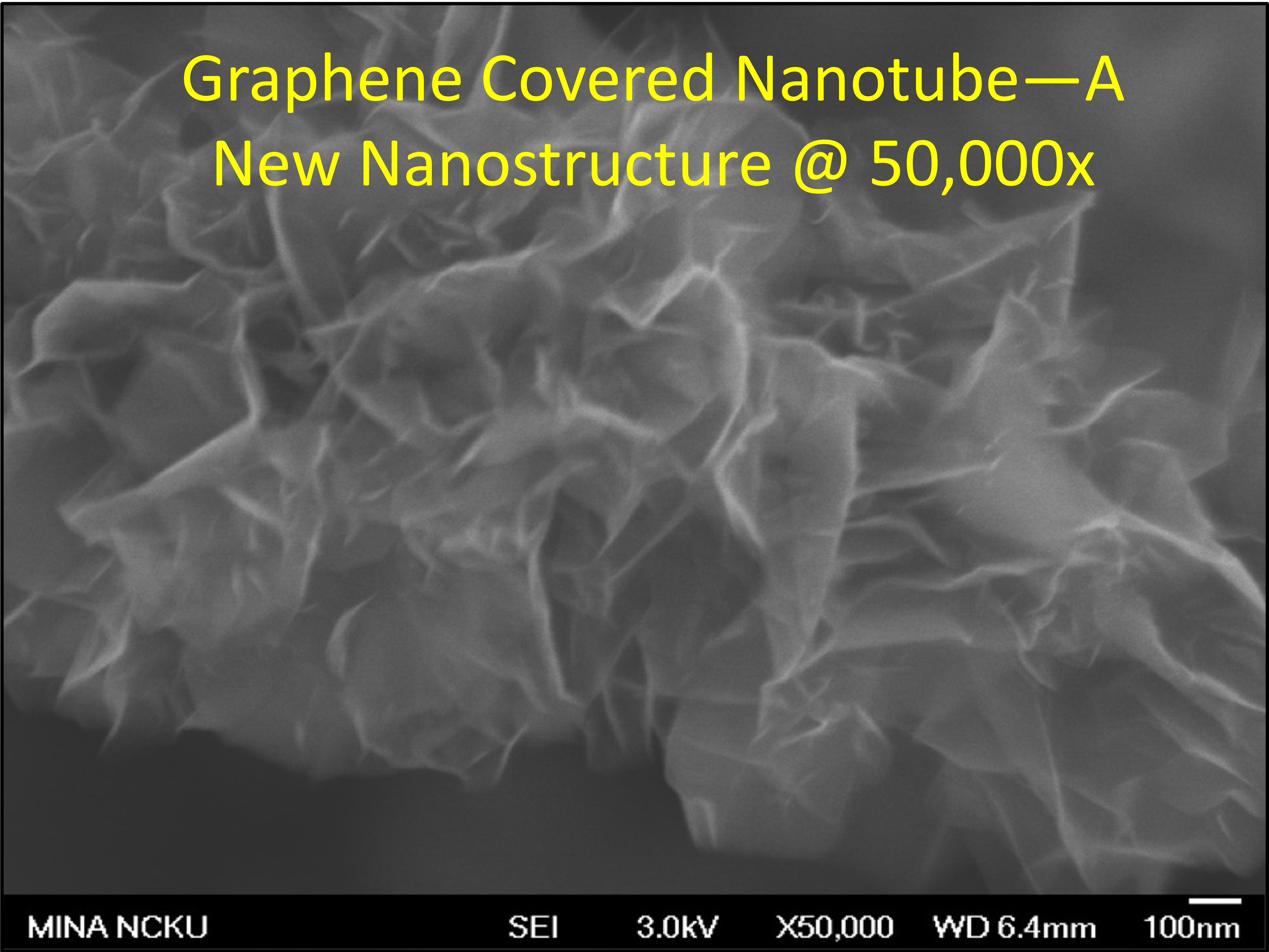



Graphene Covered Nanotubes
MINA NCKU
SEI
3.0kV
X6,500
WD 6.4mm
1μm

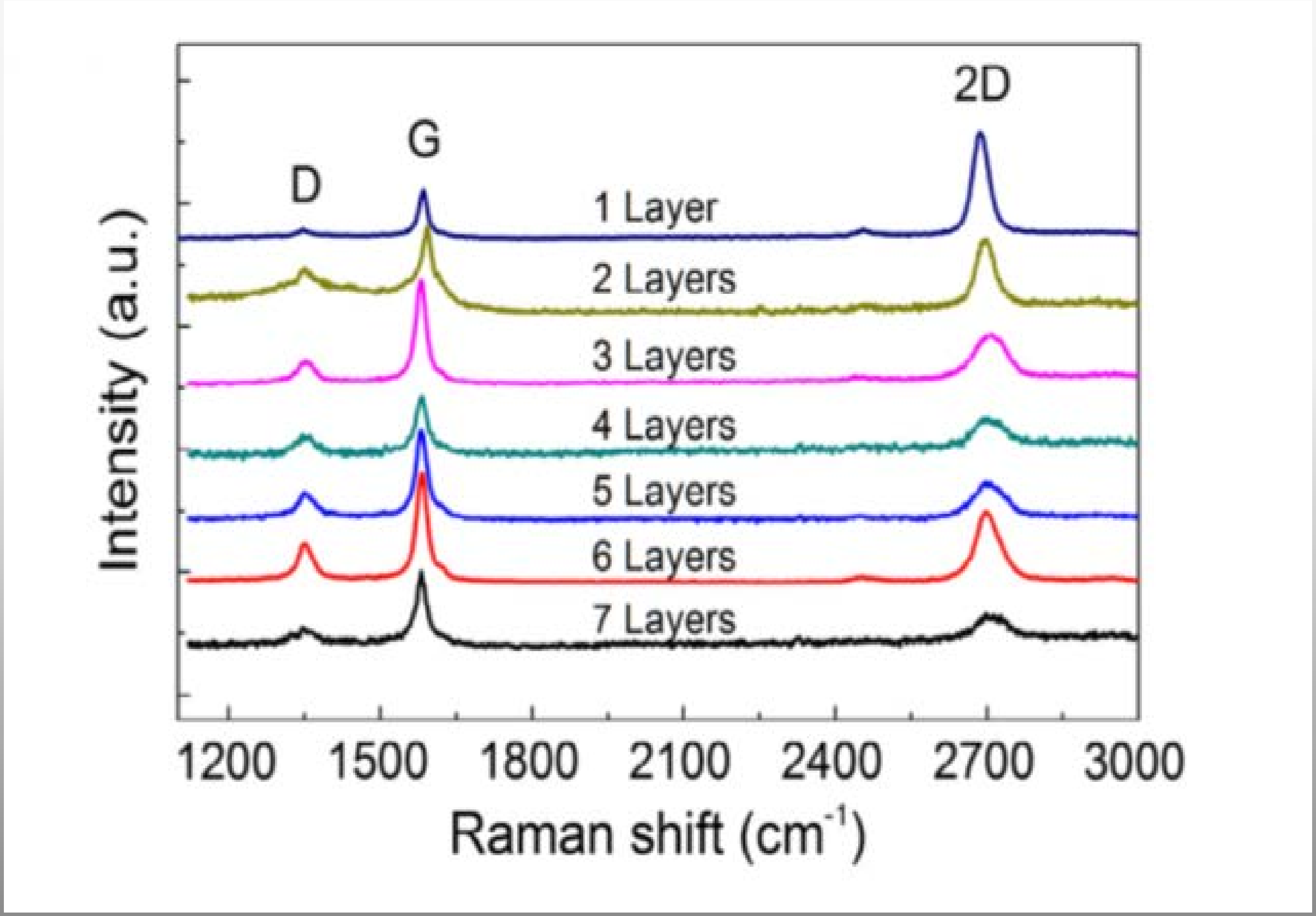
Graphene Covered Nanotube—A New Nanostructure



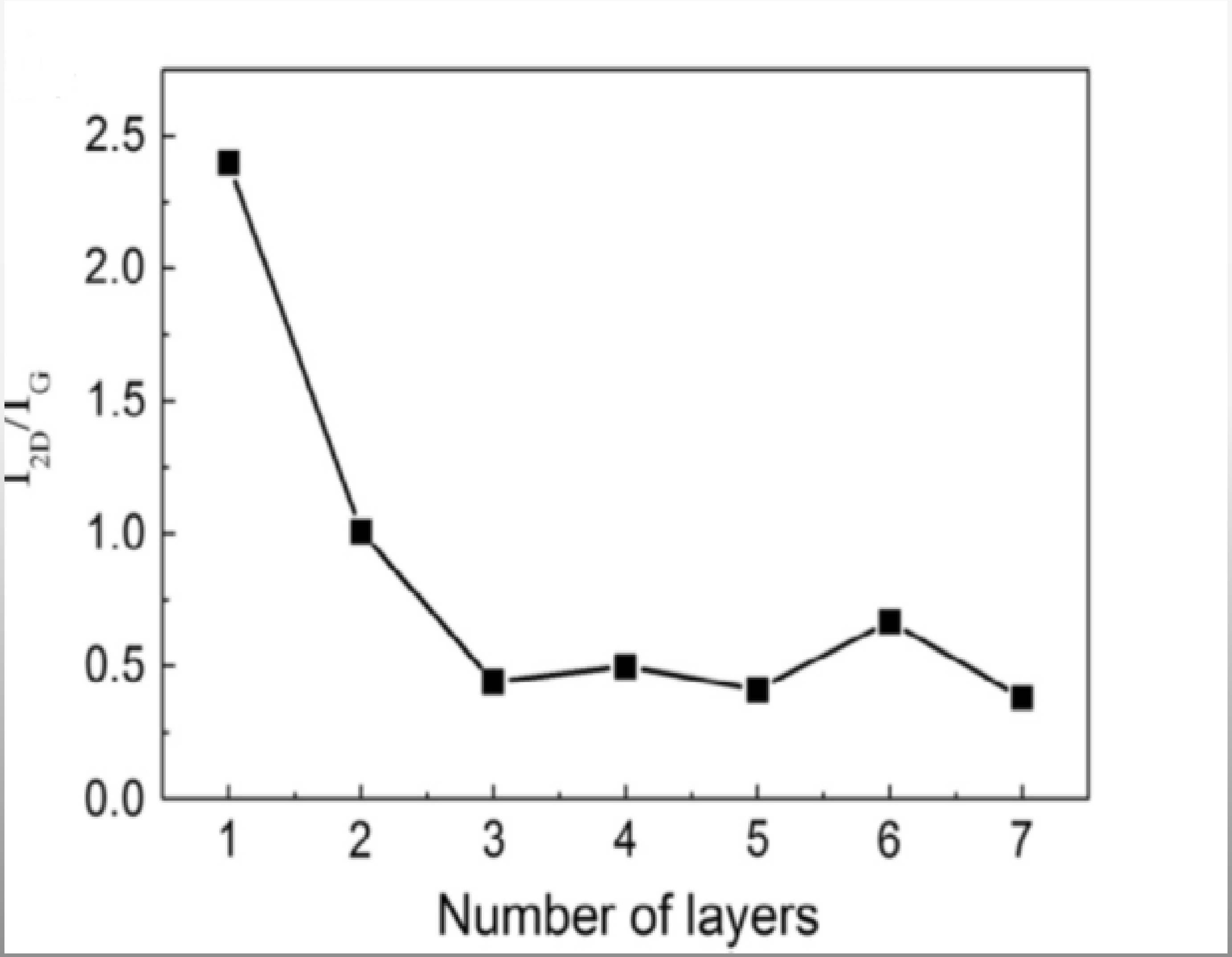
Graphene Covered Nanotube—A New Nanostructure @ 50,000x



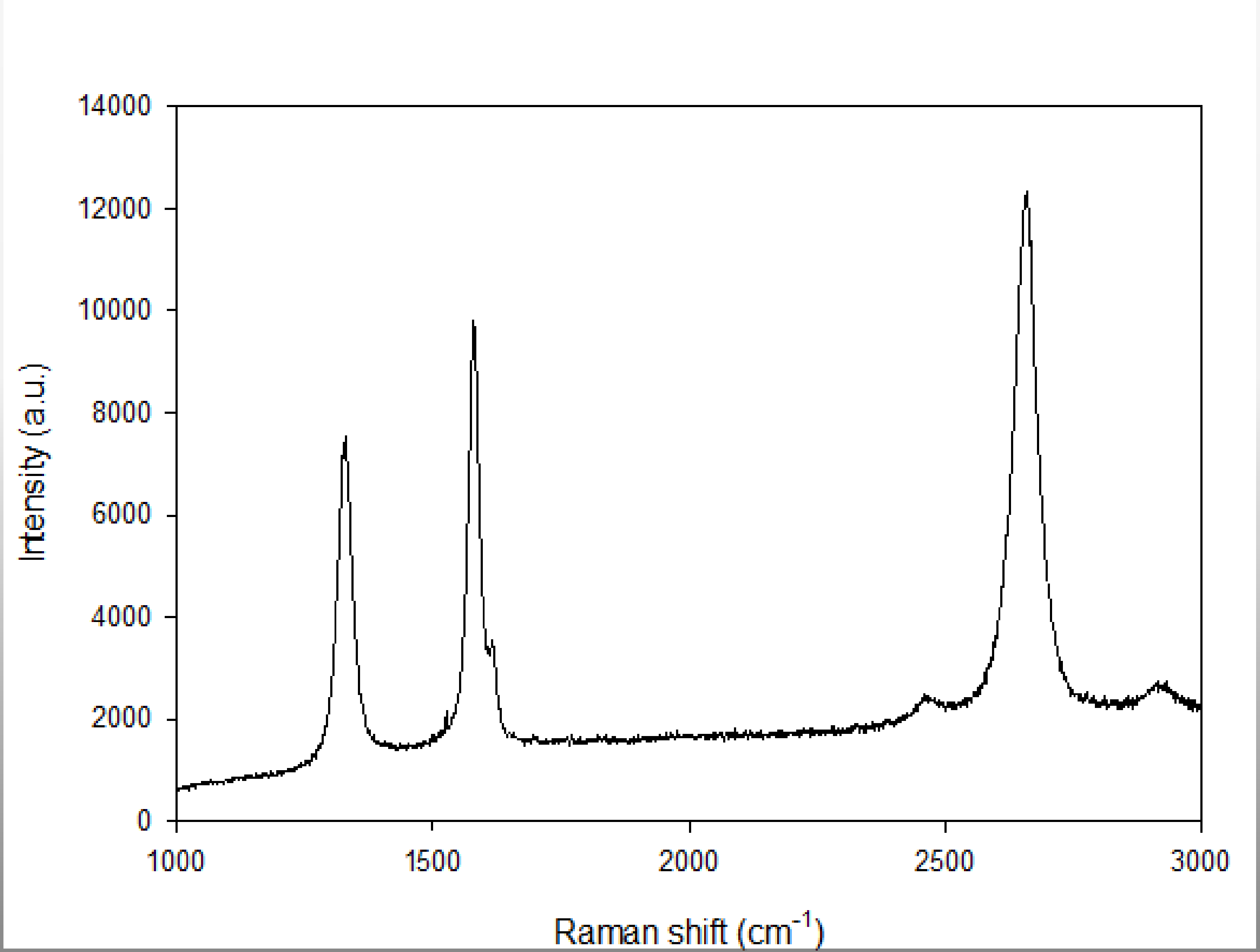
Determining the Number of Graphene Layers



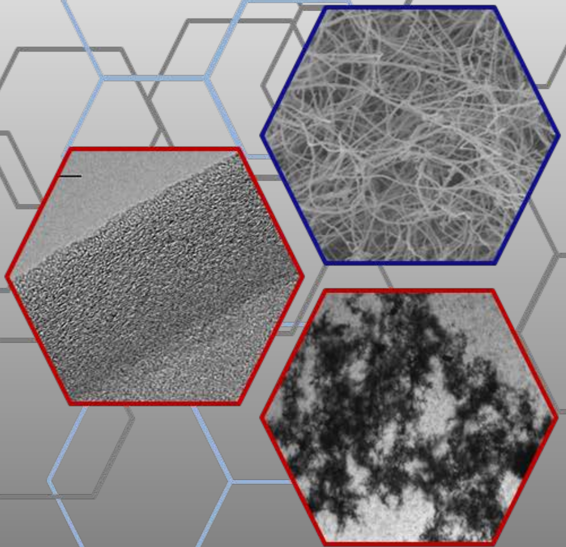
Determining the Number of Graphene Layers
Tu et al.



Estimate thickness of ASI Graphene is fewer than 2 layers



Advanced Abrasion Resistant Nanocomposite Coatings



ARC Development Current Status

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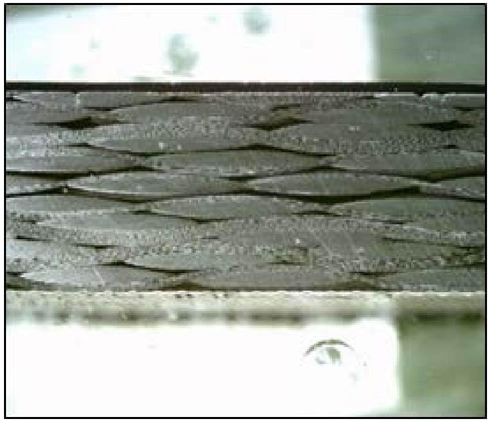
A significant need exists to develop an abrasion resistant coating for composite structures on aircraft that is capable of protecting the composite structure through use in the field and media blast coating removal operations.

- ✓ Solvent-free, spray-able coating cures in 8 hours at room temperature with a 4 hour pot life
- ✓ Abrasion resistance barrier to protect composite structures
- ✓ 90% reduction in erosion wear rate compared to the baseline primer
- ✓ Adhesion to other common materials and substrates used by US Air Force
- ✓ Withstand high temperatures;
- ✓ UV degradation and chemical resistance;
- ✓ Tailorable electrical conductivity



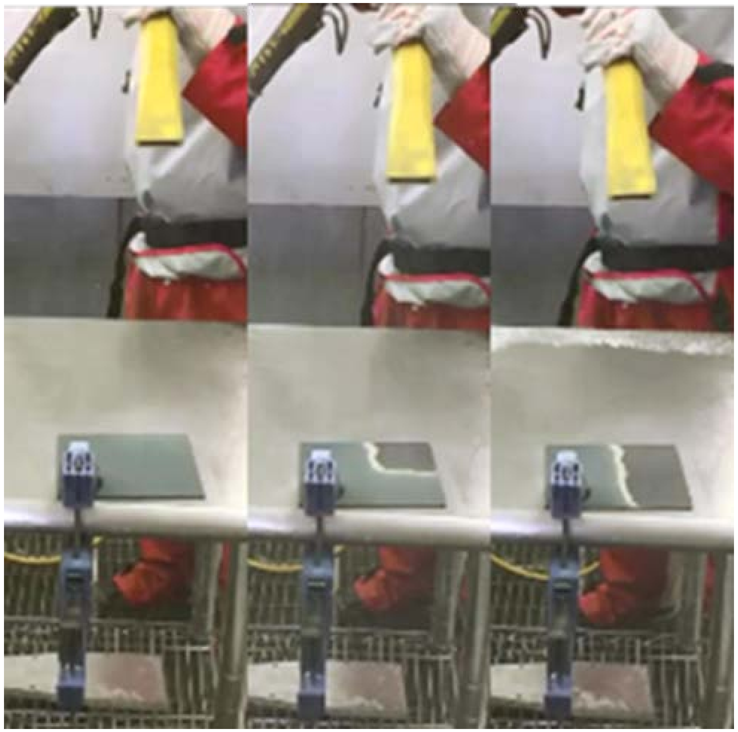
The composite coating systems meet quality and acceptance criteria for the prime contractor and processing requirements sought by Air Force while exceeding the performance specifications.

ARC Development Current Status

ASI coating systems enable consideration of more aggressive removal methods to be considered as the systems provide over an order of magnitude better abrasion protection compared to the baseline material;

Demonstrated the feasibility of using ASI coating system in high viscosity form as a hand-applied repair spackle;

Scale-up activities, as well as compatibility and survivability are under way.



Discussion and Questions

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