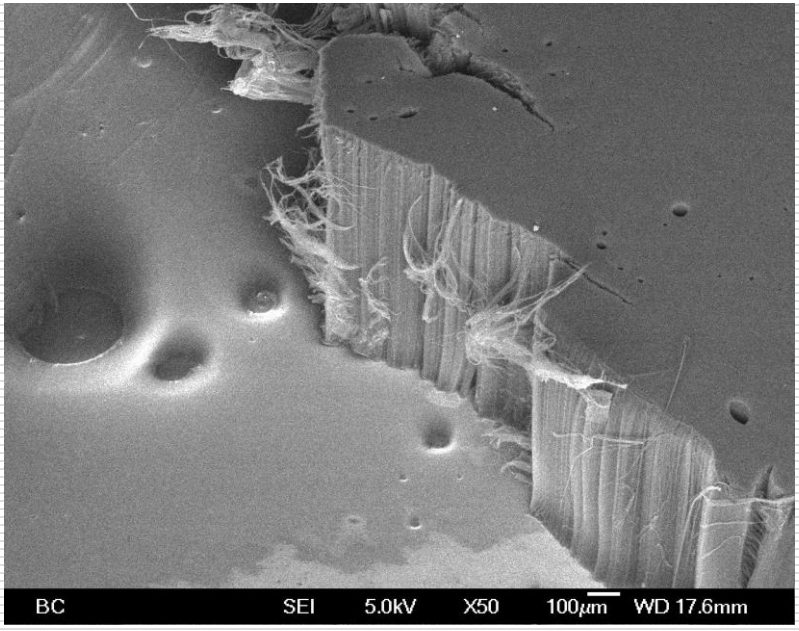
NanoLab, Inc.
Nanostructured Optical Black Coatings



Presenter: David Carnahan

Contents

- NanoLab overview
- Introduction to nanotube-based black coatings
- NanoLab optical black coatings
  - **adVANTA Black**
    - 2-step processing: catalyzation & CVD growth
    - Properties + applications
  - **Singularity Black**
    - Solution-based coating process
    - Properties + applications

Introduction to NanoLab

- NanoLab has recognized expertise in:
  - nanomaterials fabrication,
  - nanocomposite formulation, and
  - Nano-product & process development
- Domestic *manufacturer* of carbon nanotubes and supplies a variety of carbon nanotube products to industrial and academic customers.
- Contract research and *product development* activities for governmental and industrial customers that require products with tailored material properties or unique functionality.
- *Coating services* for optical parts

NanoLab Capabilities

Nanomaterial Synthesis

- Air-free chemical synthesis
- Hydrothermal synthesis
- Full wet chemical lab
- CVD reactors
- In-house CNT production & functionalization
- Plasma & ozone etching
- Electrochemical deposition
- Access to:
  - E-beam lithography
  - Full clean room
  - Metrology & SEM Lab

Product Design Tools

- Eagle (circuit board design)
- Solidworks (3D drafting)
- LabVIEW (DAQ & process automation)
- 3D printing and prototyping

Plastics, elastomer & epoxy composite tools

- Lab-scale extrusion line
- Two and three roll milling
- Centrifugal mixing
- Resin transfer molding & ovens

Inks & Paint Formulation Tools

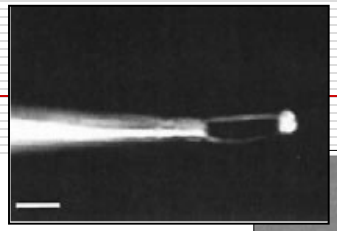
- Ultrasonic dispersion equipment
- Screen & inkjet printers, and drop-on-demand printing
- Spray booth, clean hoods

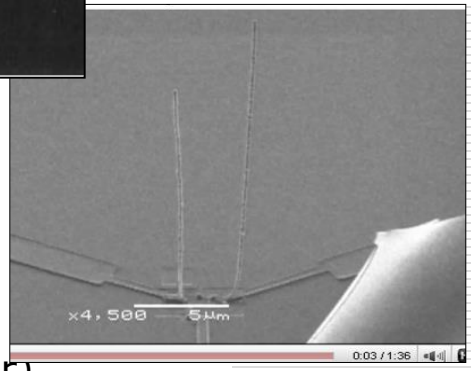
Characterization

- Optical
  - FTIR
  - UV-VIS-NIR
  - Raman
- Thermo-physical
  - TGA
  - DSC
  - DTA
- Mechanical
  - Tensile
  - Impact
  - Adhesion
- Electrical
  - Resistance
  - Impedance
  - Capacitance
  - Inductance

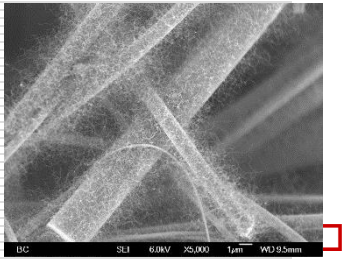
Material systems: carbon nanotubes, nanoparticles & nanowires of oxides, metals, carbides
Matrices: epoxies, silicones, rubbers, urethanes, polyimides, metals, carbides, oxides

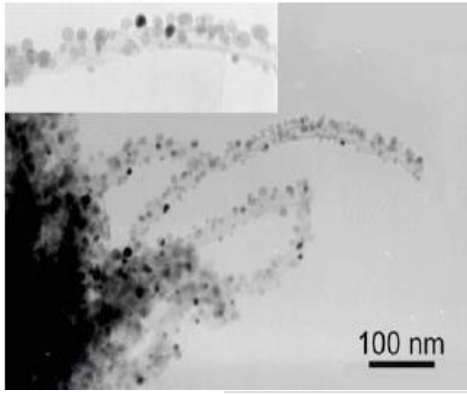
Technology portfolio

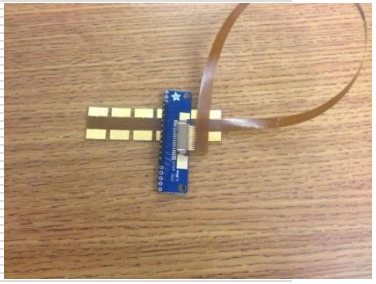


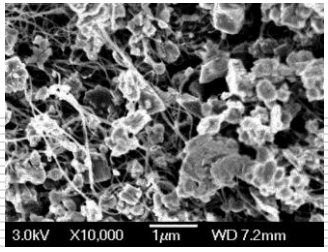


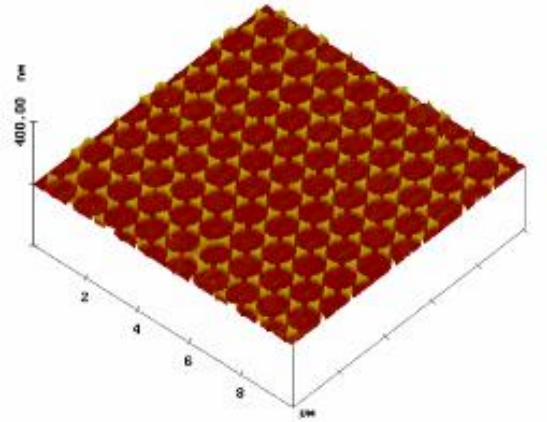
- Sensors & tools
  - Nanoscale tweezers/grasping tools
  - Radiation, gas sensors (Private)
  - Wear sensors for bearings (Navy, NHBB)
- Composites
  - Toughened B_4C armor nanocomposites (Army)
  - CNT-reinforced epoxy composites (Schlumberger)
  - Elastomeric strain sensors (Adidas)
  - Filtration media for virus removal (Lydall)
- Coatings
  - Catalytic nanoparticle coatings (DOE)
  - Corrosion resistant coatings & primers (Navy)
  - Low Z scintillator coatings (Private)
  - Photonic lattices
  - Optical black coatings (NASA)





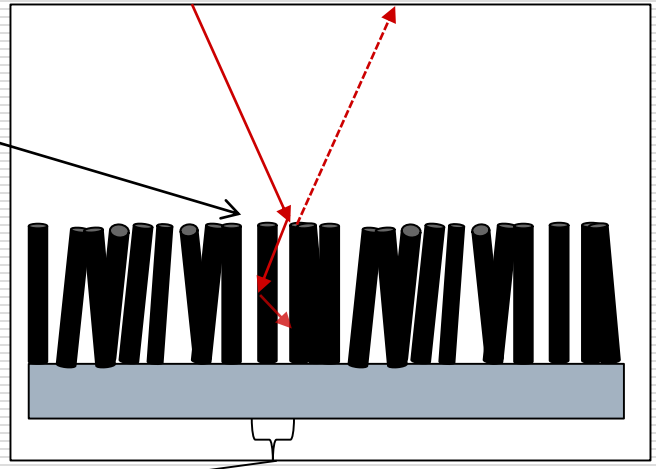


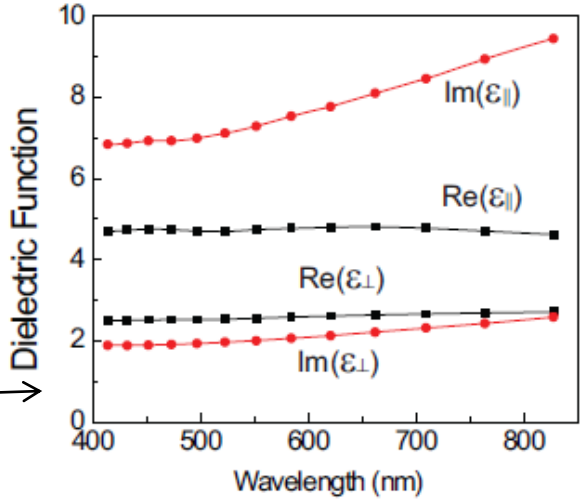


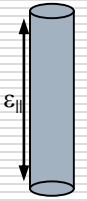


What makes a good black surface?

- **Minimize Reflection**: Coating must match the refractive index of the atmosphere above it.
  - Nanotube arrays are sparse, low volumetric density (~5vol%) structures.
- **Provide long total path length** for absorption…A coating should be 2-3 wavelengths thick at the wavelengths we care about.
  - CNT lengths >> λ for optical & IR.
- **Provide short path length between inelastic interactions**.
  - Site density/spacing between CNT < λ
  - Low conductivity = high loss for CNT.
- **Flat Dielectric function**
  - As a function of wavelength





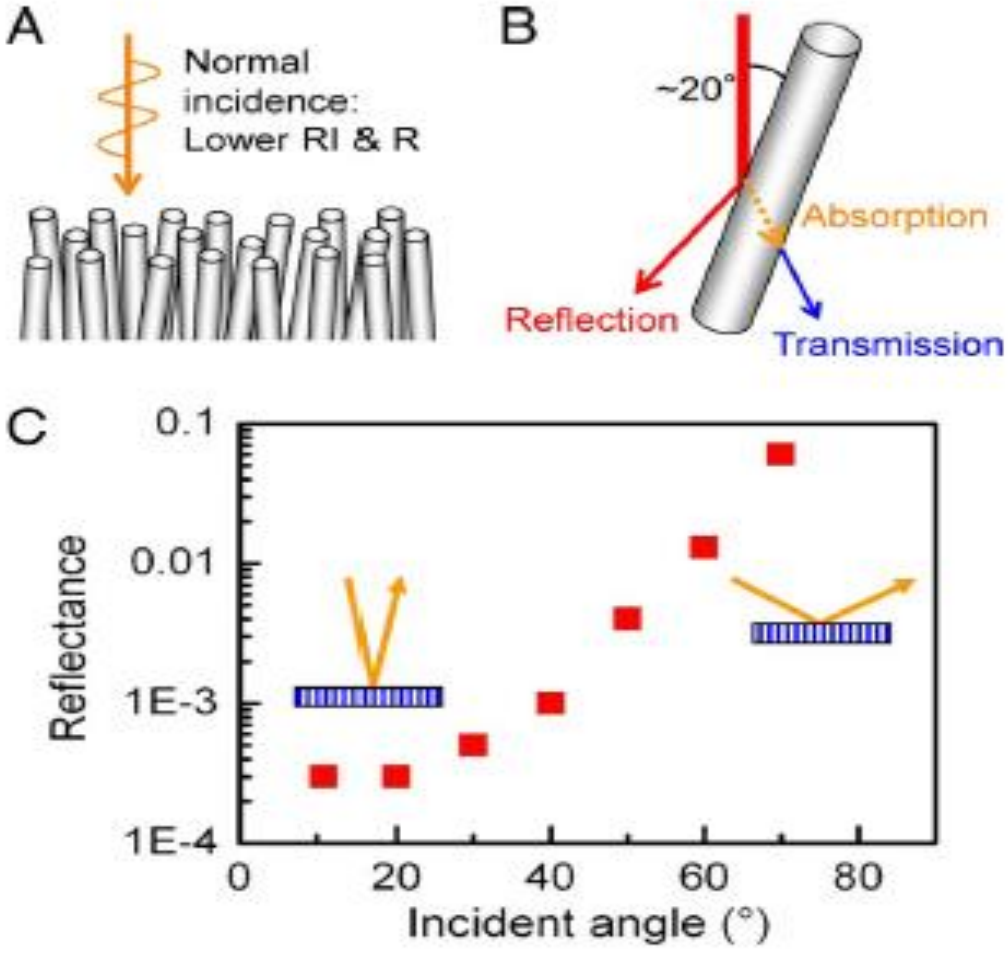


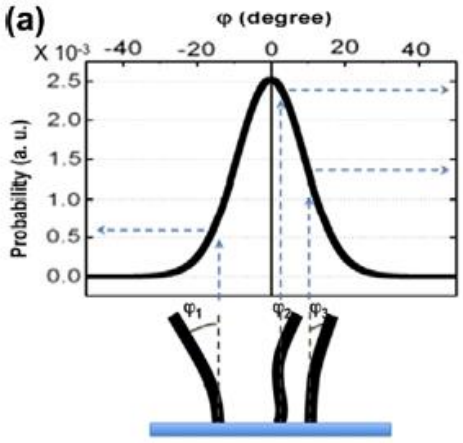
Hua-Bao, Xiu Lin Ran, Timothy Fisher, "Optical properties of vertical arrays of multiwalled carbon nanotubes from FTDT simulations" 15 March 2010 / Vol. 18, No. 6 / OPTICS EXPRESS 6353

Structure makes a difference

The optical properties of nanotube arrays to their growth parameters; determining the influence of:

diameter
site density
alignment
length
graphitization





Ref: Mizuno PNAS, 2009, 106, 15
Enhanced optical absorption cross-section characteristics of multi-wall carbon nanotubes, C. Ni, P.R. Bandaru, Carbon 47 (2009) 2898 –2903

NanoLab Optical Black Products

- NanoLab offers highly black nanotube coatings that are:
  - Applicable to multiple substrates materials
  - Conformal to complex parts of any size
- ***adVANTA***™
  - Materials are catalyzed by sputtering or wet catalysis, and Vertically Aligned NanoTube Arrays (VANTA) are grown directly by Chemical Vapor Deposition (CVD) ~700C
  - Gives best blackbody optical performance from UV to IR
  - Can be transferred onto other substrates

- ***Singularity***™ Surface is a paint, directly coated with un-aligned carbon nanotubes in a matrix.
  - Easily masked and applied as spray formulation
  - Outperforms SOA materials
  - Activated by 250-300°C processing
  - Frangible, but robust
  - Recoatable

adVANTA Processing

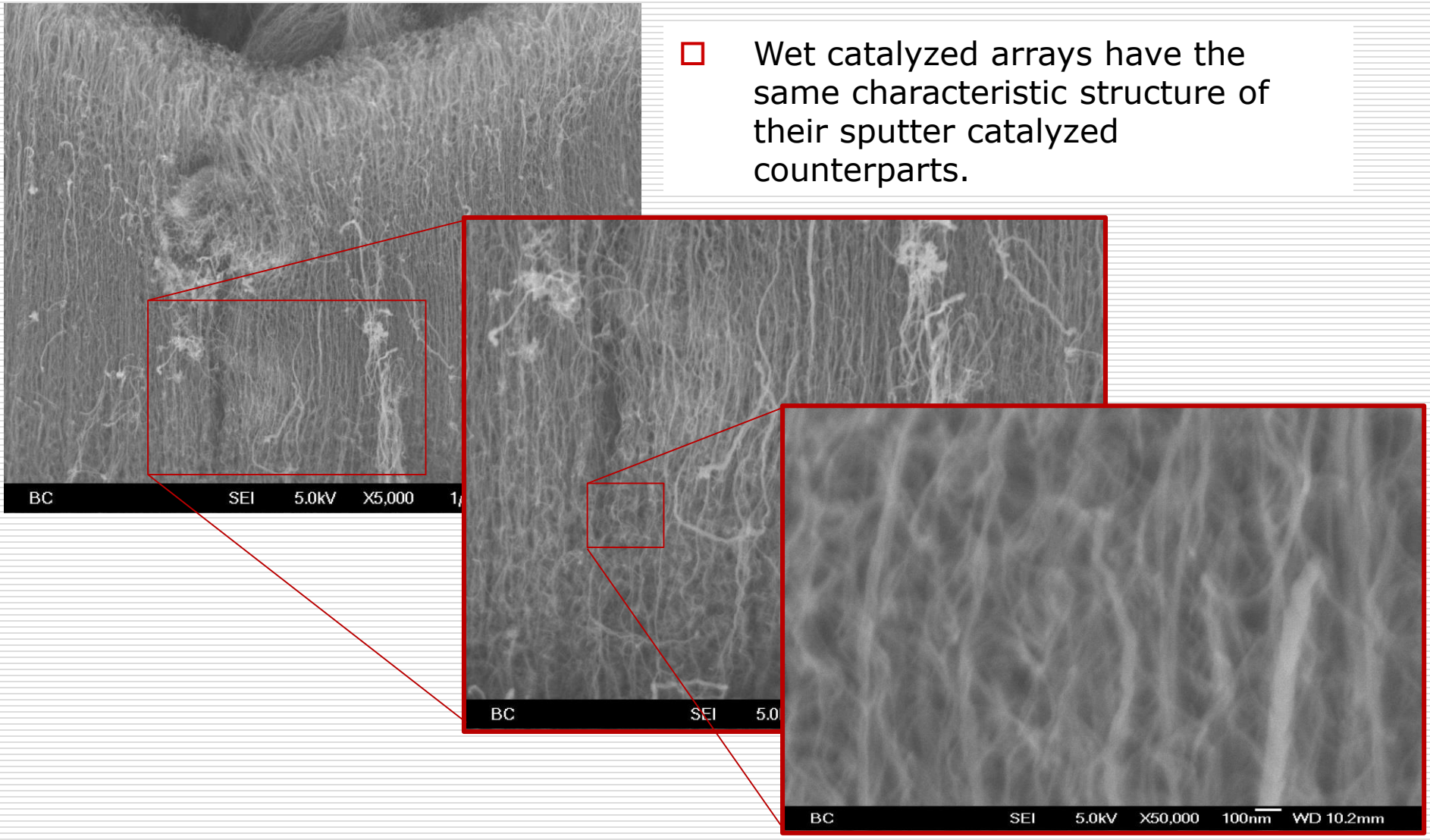
- Standard catalysis Al_2O_3 +Fe:
  - Sputtering or Evaporator
    - 10$/m^2 at large volumes
    - Line of sight deposition
- Wet chemical approach
  - Spray or Spin Coating
    - ~$1/m^2 at volume
    - Good for complex parts

Chemical vapor deposition: ~700C, Ar, H_2, C_2H_4

Finished component

adVANTA microstructure.

- Wet catalyzed arrays have the same characteristic structure of their sputter catalyzed counterparts.



Wet catalyzed adVANTA on complex shapes

- adVANTA coatings have been successfully grown on every substrate attempted to date that support the growth temperature.

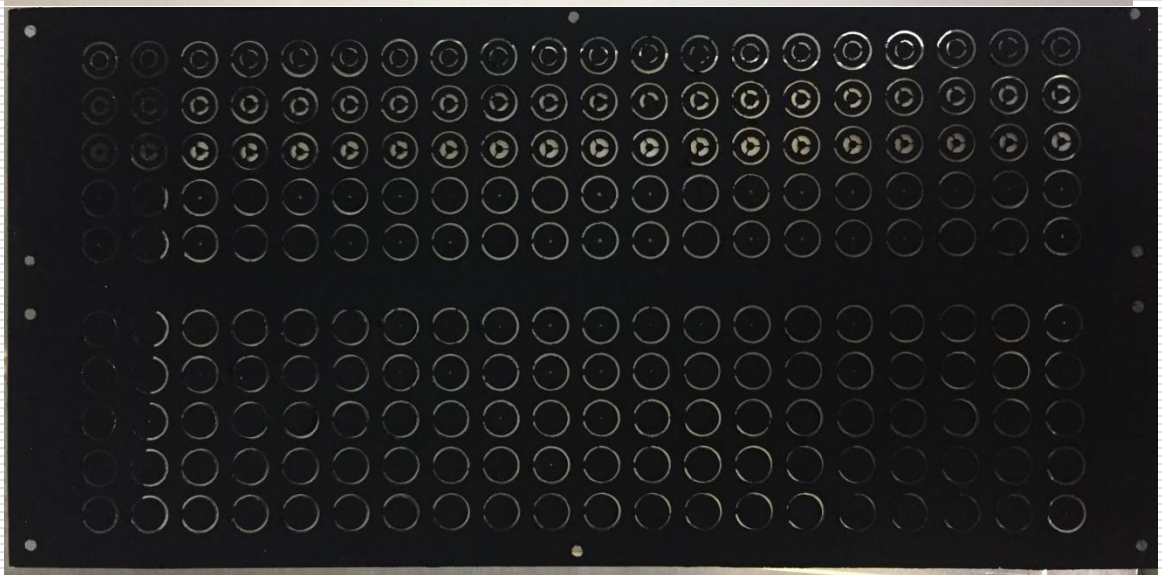
BOLTS- ¼-20

HEAD ONLY

FULL COATING

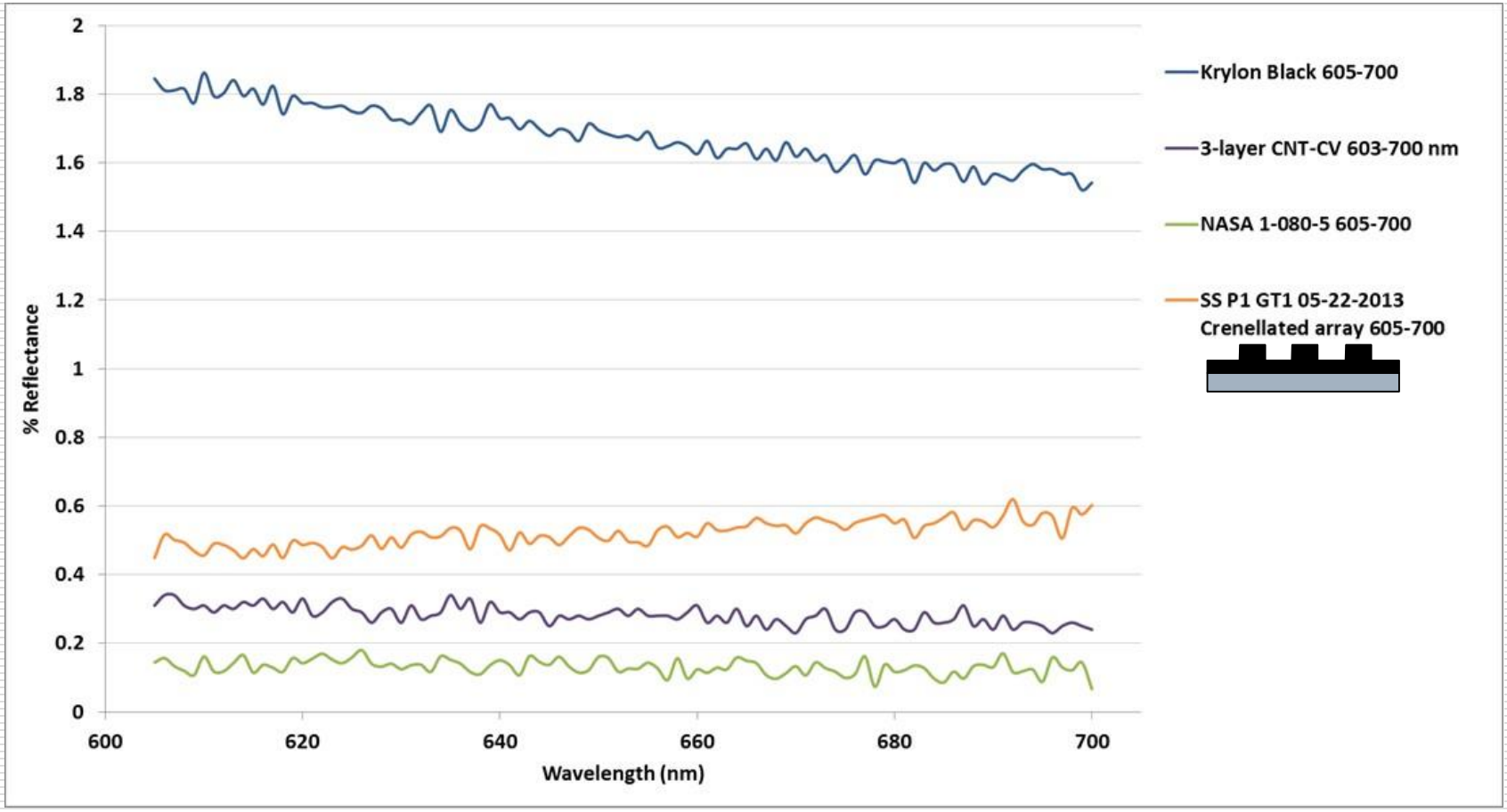
AS RECEIVED

APERTURE SHEET

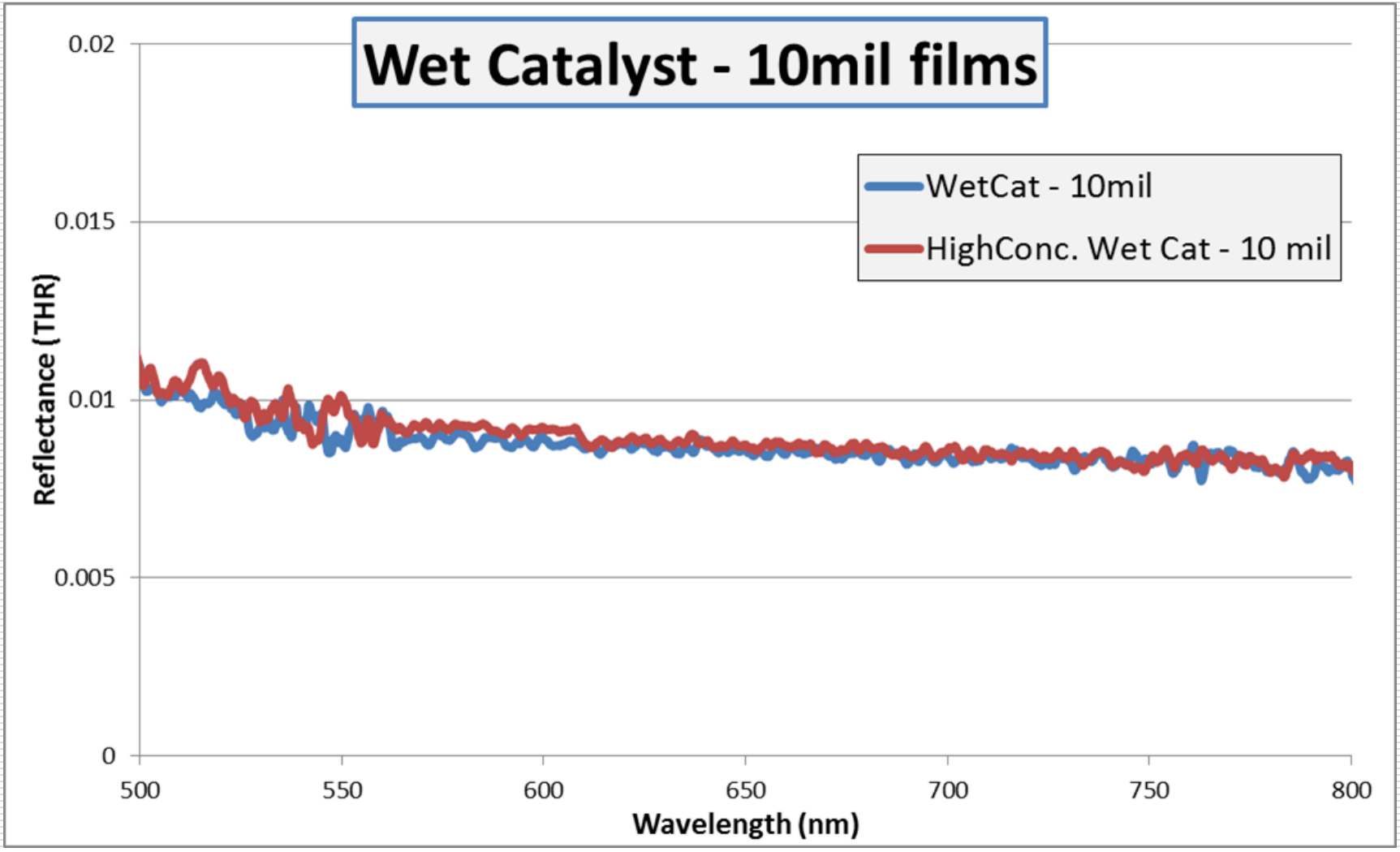


adVANTA UV-Vis Data

- Optimized coatings exhibit 0.1% THR in the optical range.
  - PE Lambda 19, with integrating sphere



THR Optical performance of adVANTA



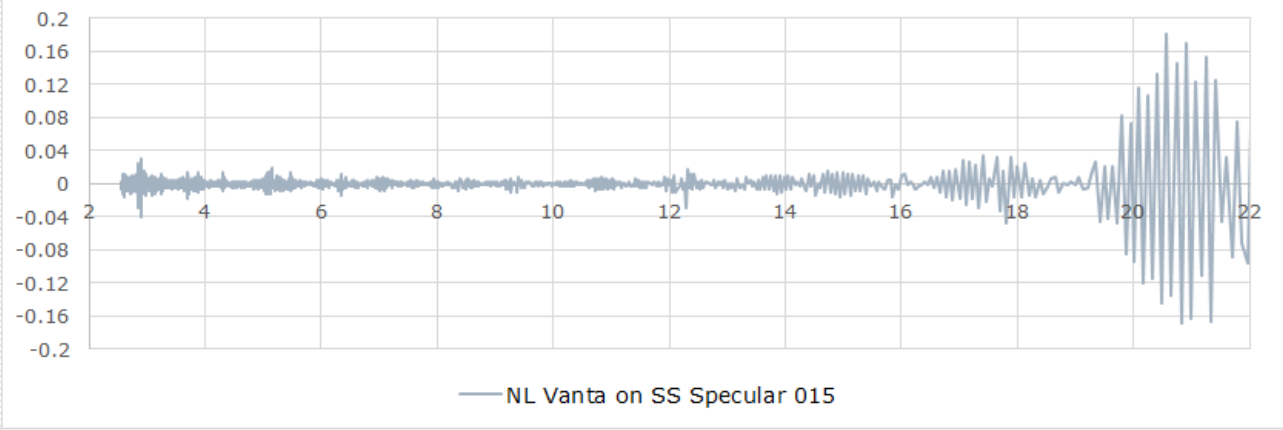
- UV-Vis reflectance data for liquid-phase adVANTA catalyst deposited by metering bar. Reflectance of ~1% is seen in the visible range.

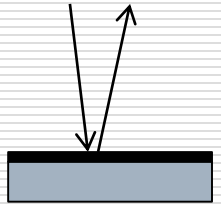
Longer wave IR Measurements

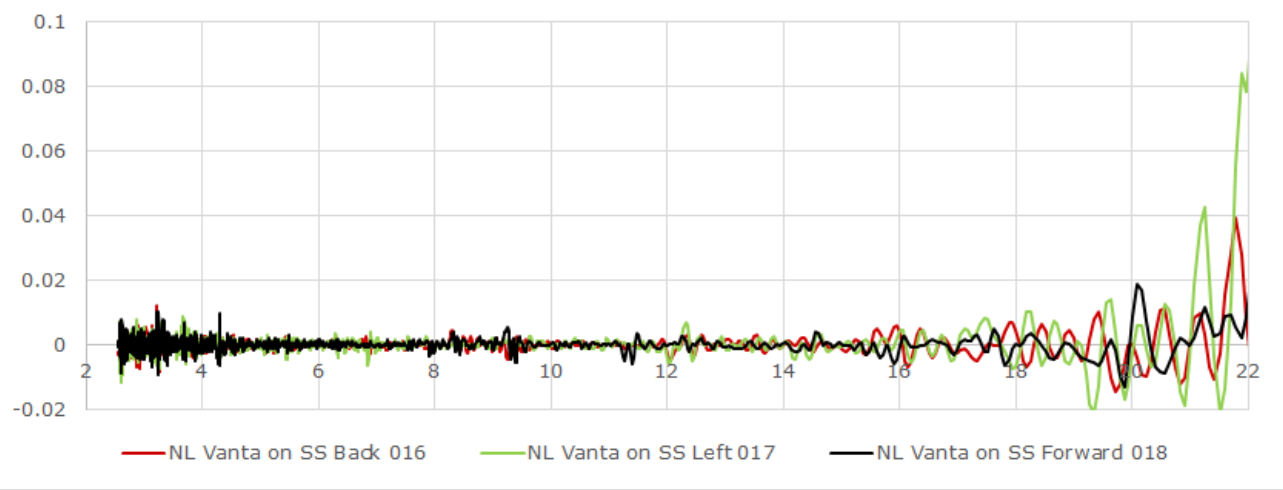
- Made at Low Background Infrared (LBIR) facility, NIST, 2017, A. Carter.
- Measurements made with a Bomem DA-8 using a reflectance rig, sample illumination with f/4 cone.
- Reflectance measurements were made in specular and non-specular configurations.
- No sphere based total integrated scatter (TIS) measurements were made, as the reflectance for many of the samples was so low that signal to noise was relatively poor.
- For specular measurements, angle of incidence (AOI)~15°.
- For non-specular measurements (used to characterize the diffuse component of reflectance), the sample was tilted X degrees from the specular position either backward, forward, to the left, or to the right.

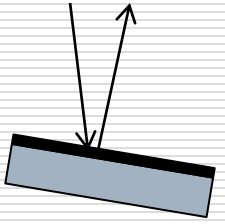
adVANTA Specular Reflectance

- 3-22 microns

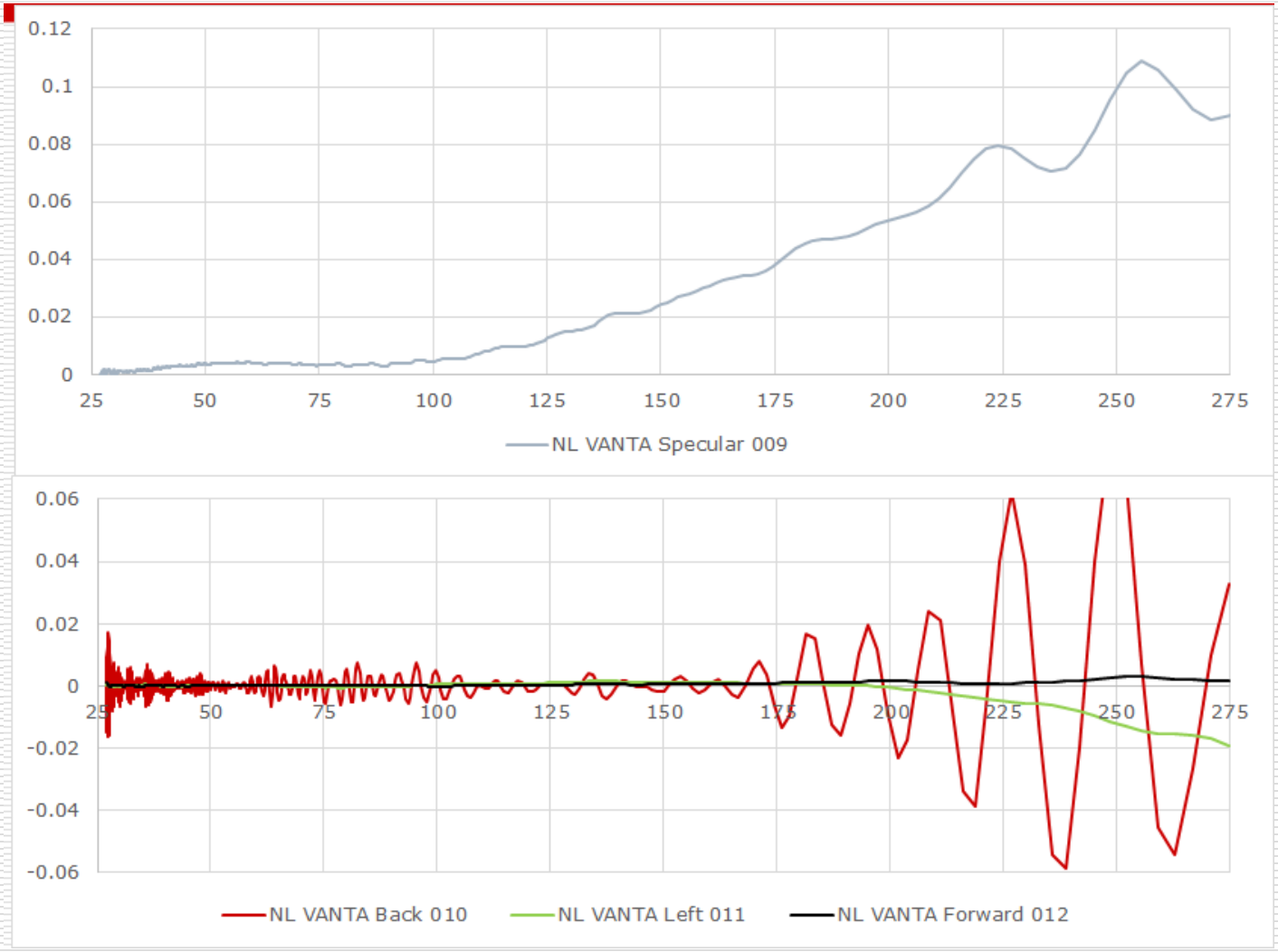




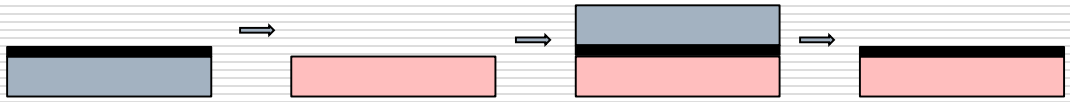


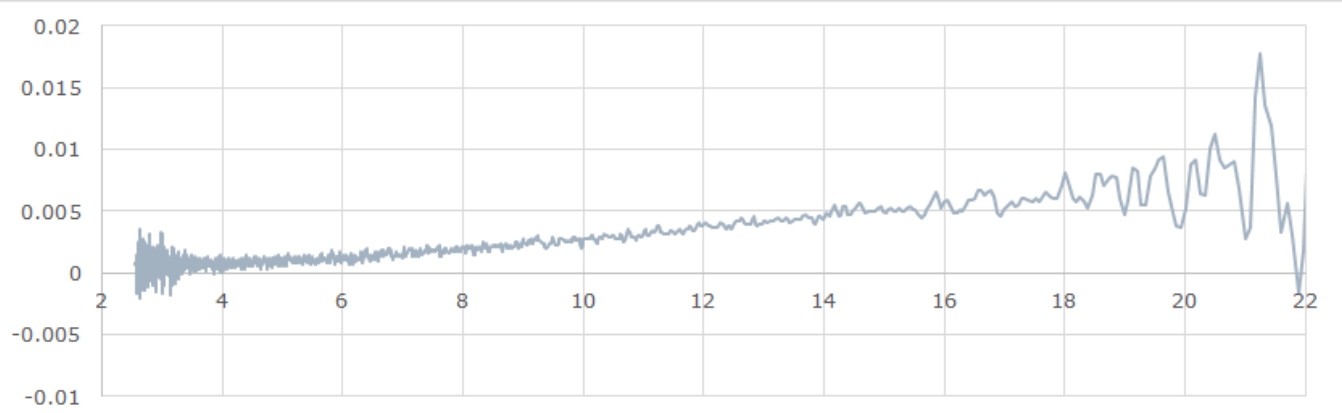


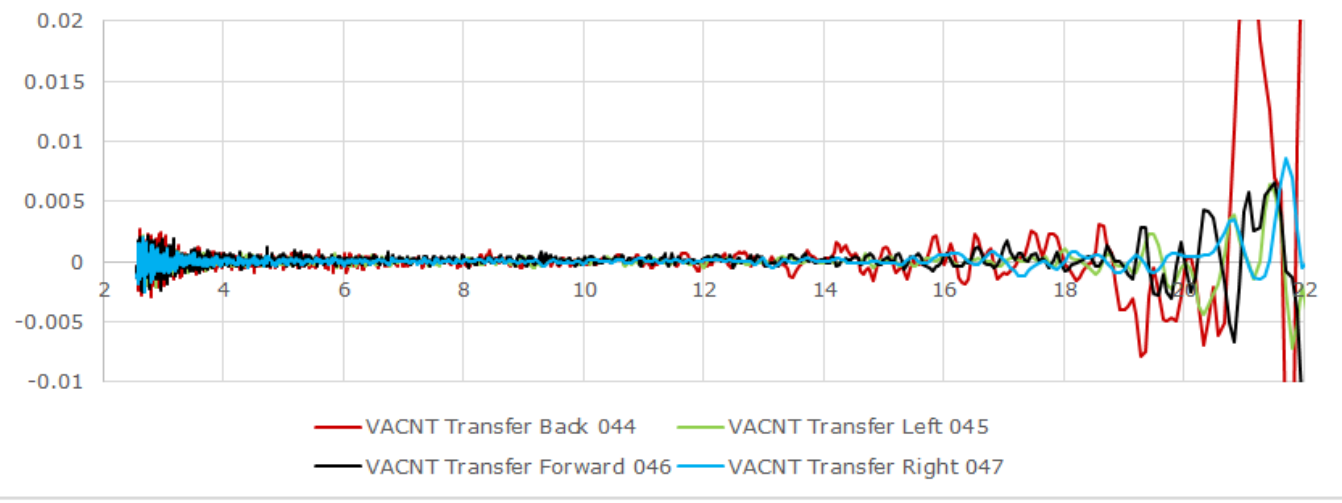
adVANTA Specular Reflectance 25-275um



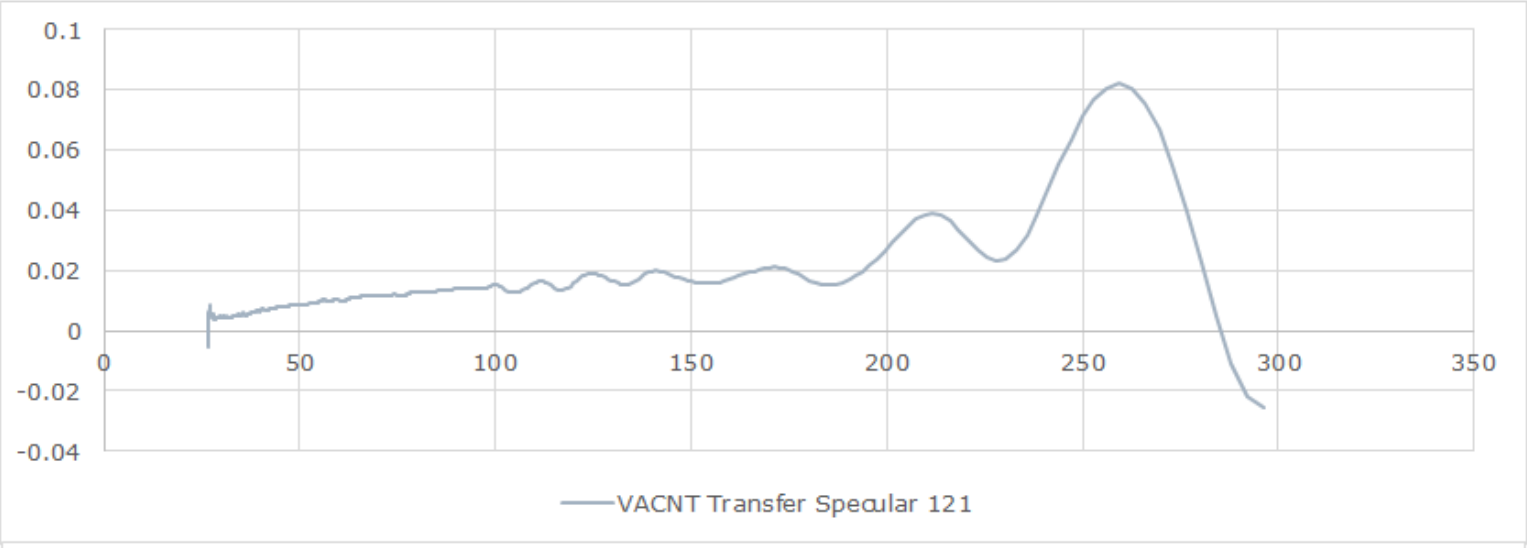
adVANTA Specular Reflectance- transfer

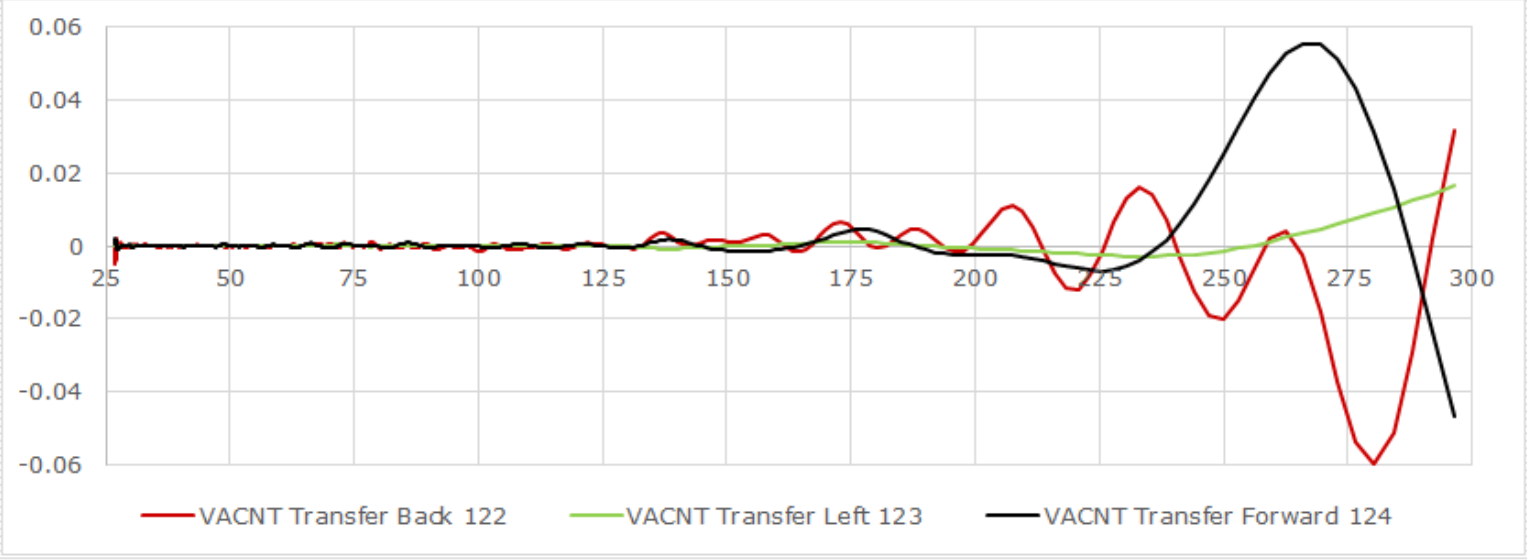






adVANTA transferred array - Specular Reflectance

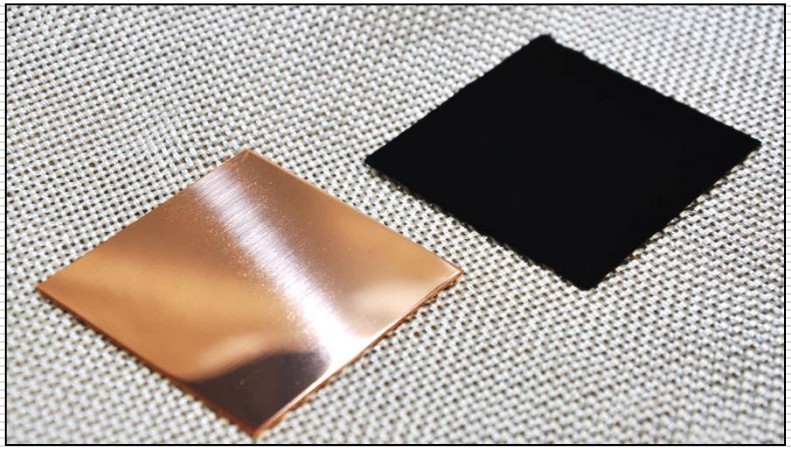


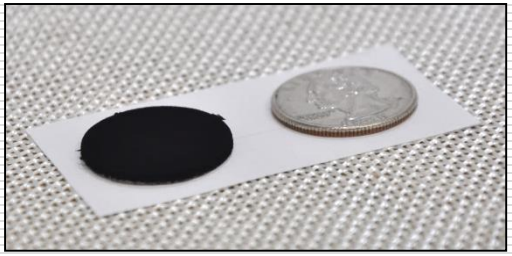


Singularity Black paint

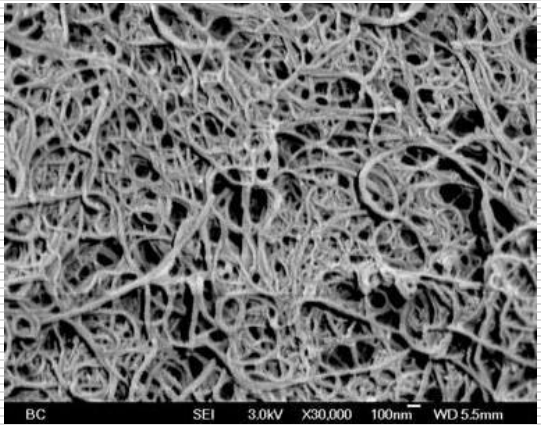
- Why do we need this?
  - Temperatures of the CVD process are not suited to aluminum, plastics or composites
  - We need an approach that is not limited by furnace sizing.
- Our challenges were:
  - How to retain the low density network?
  - How to keep any thermal processing below ~300C?
  - Can these be sufficiently black, and well adhered?
  - Could these coatings be repairable?

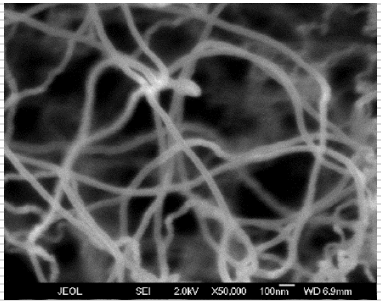
Super Black!



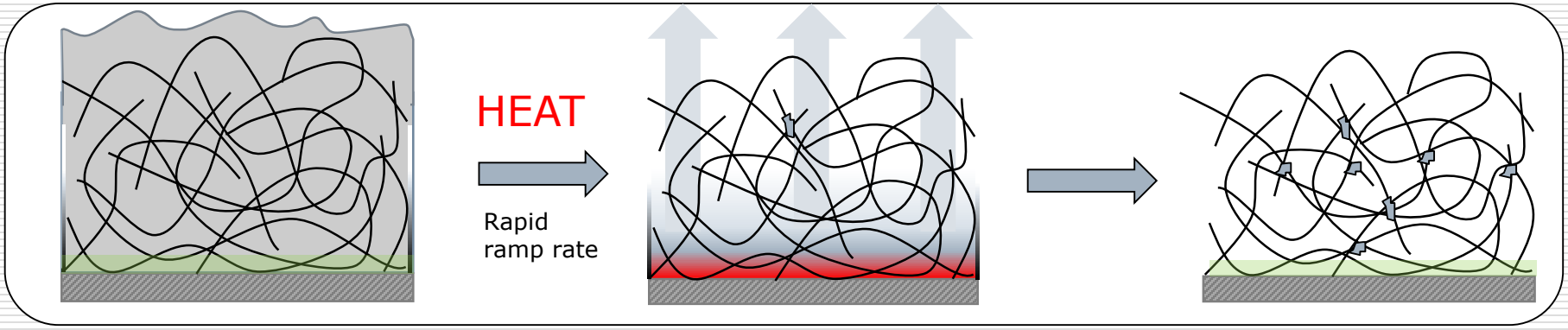


https://youtu.be/9_KyBalghFg

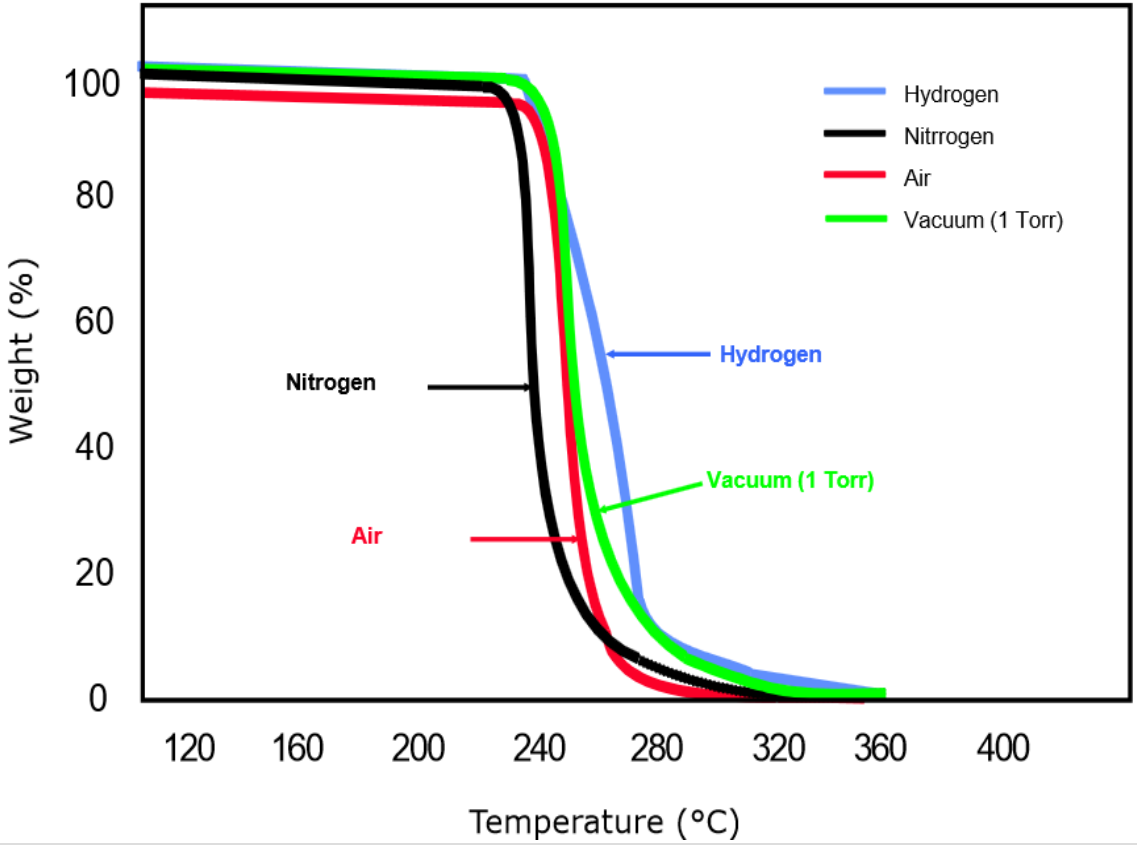




Singularity Black thermal processing



- Thermal processing removes binder to yield low-density CNT coating
- CNT interlocked and bonded to substrate
- < 10 ppm residue after burn off at 300°C



Singularity Black sample parts

Kapton™ Polyimide

Aluminum foil

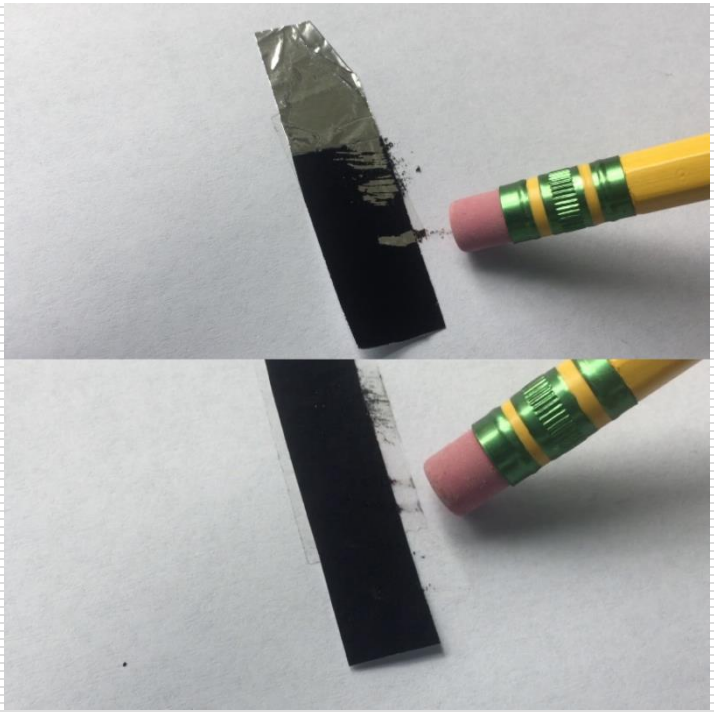
aluminum mount

Aluminum aperture

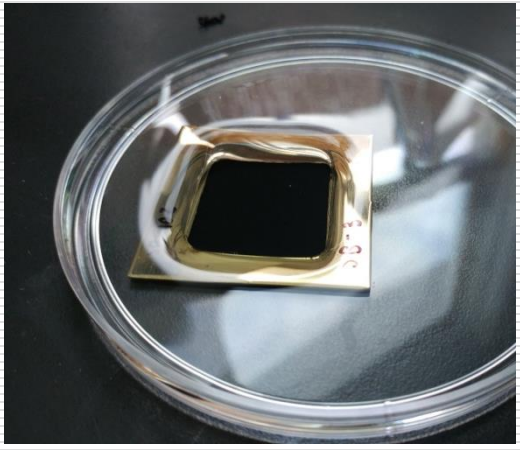
Laser sintered titanium baffle

Singularity Black with Adhesive Primer

- Pristine Singularity Black coatings are sensitive to physical rubbing or scratching
  - Common problem in CNT-based black coatings
- Adhesive primer improves abrasion resistance of Singularity Black coating
  - Able to withstand incidental rubbing or contact during handling

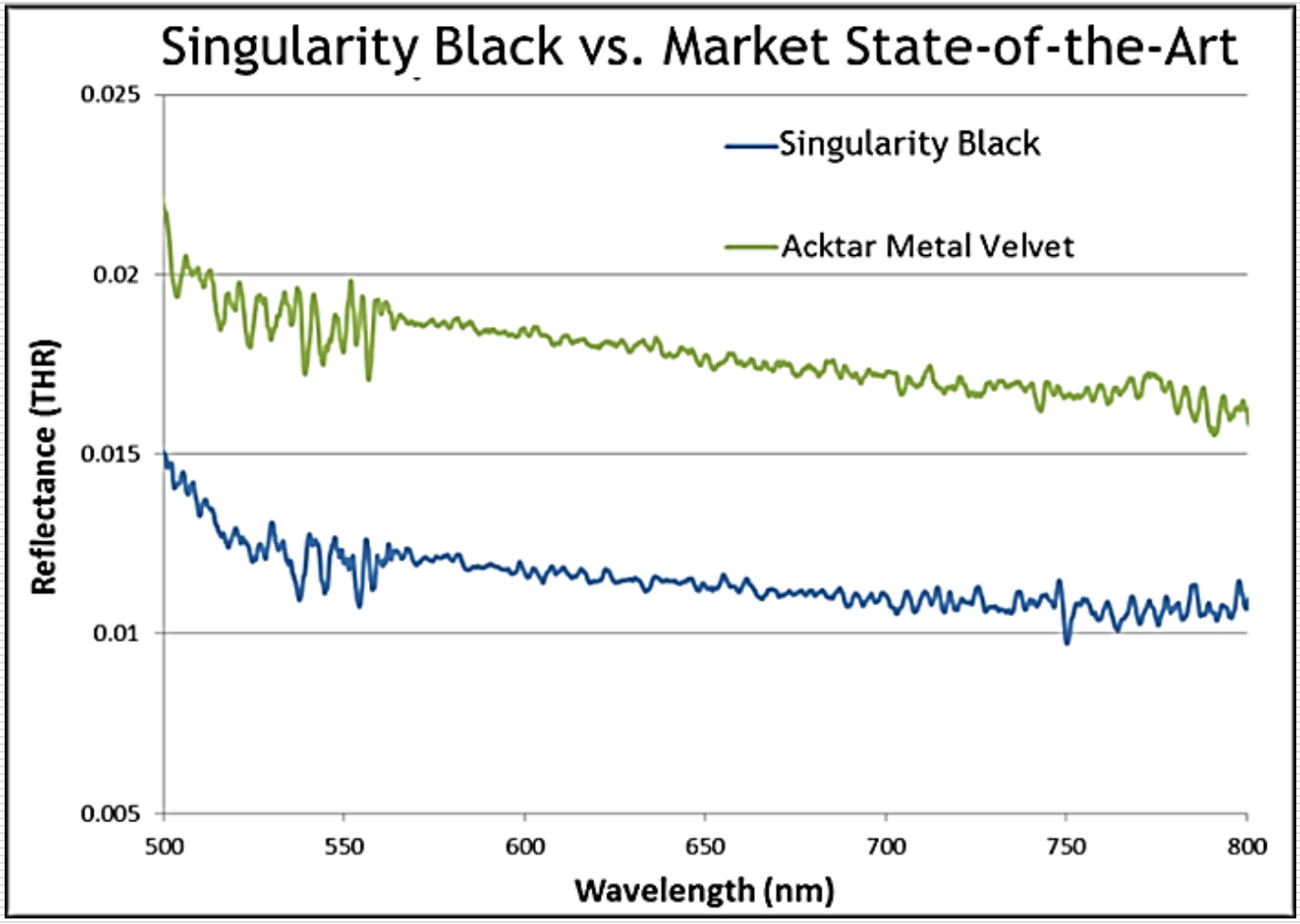


https://www.youtube.com/watch?v=qFCGEtu_1mA



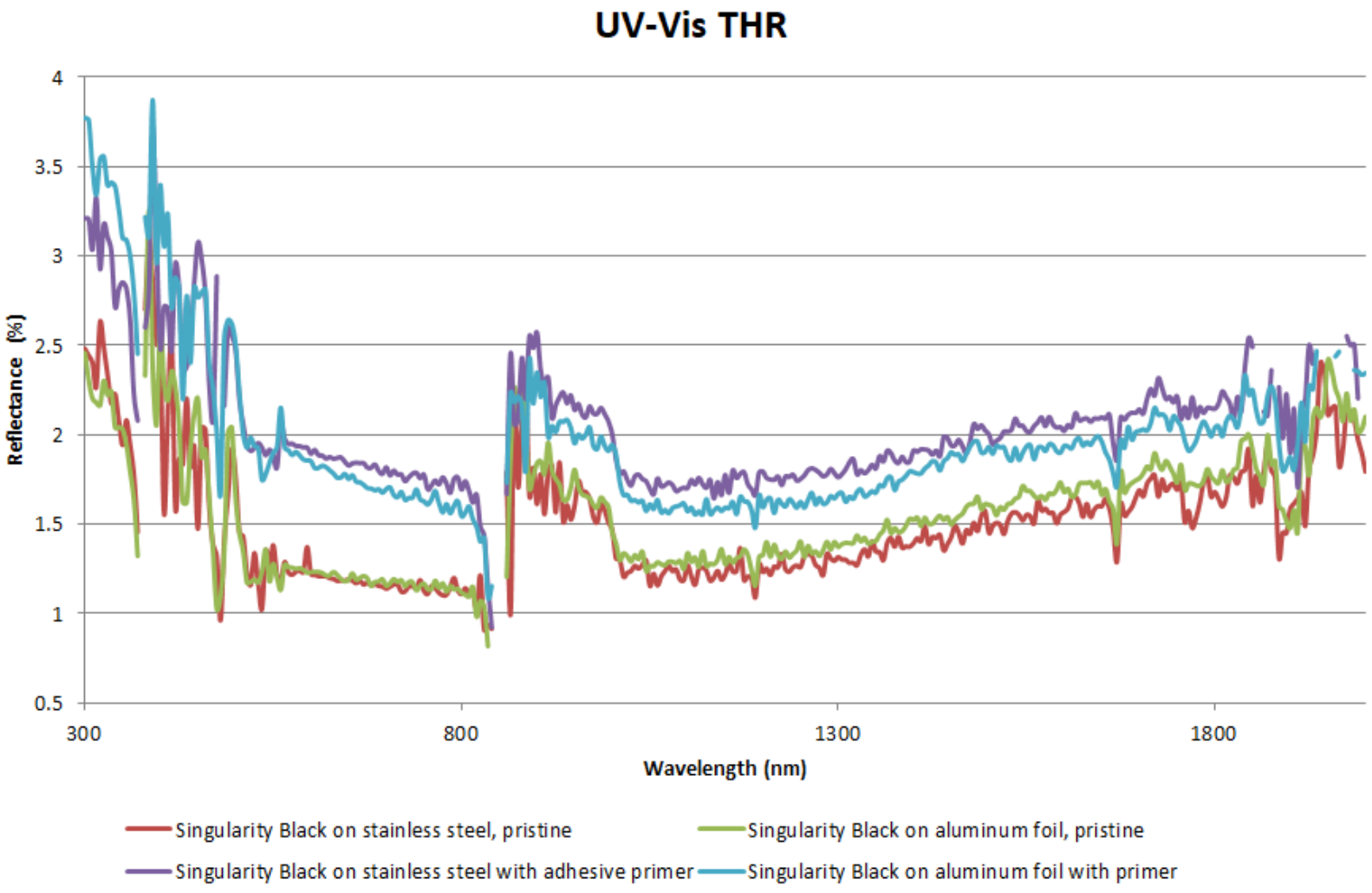
Also now hydrophobic!

Singularity UV-VIS- Total Hemispherical Reflectance



- UV-Vis spectra of reflectance of Singularity Black coating compared to Acktar Metal Velvet.

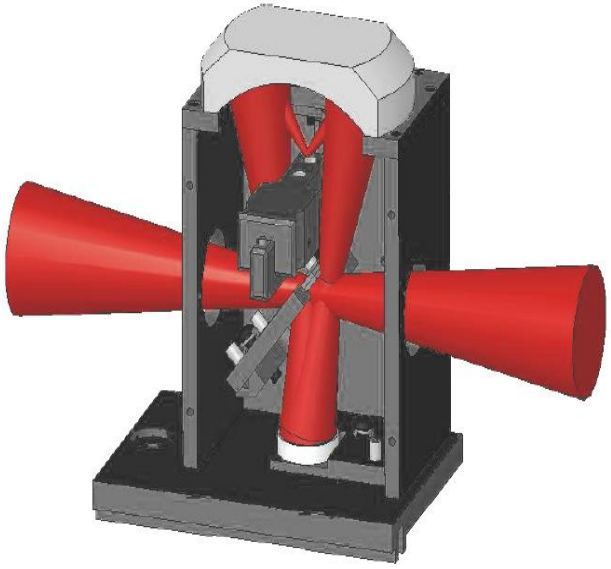
UV-Vis-NIR Reflectance



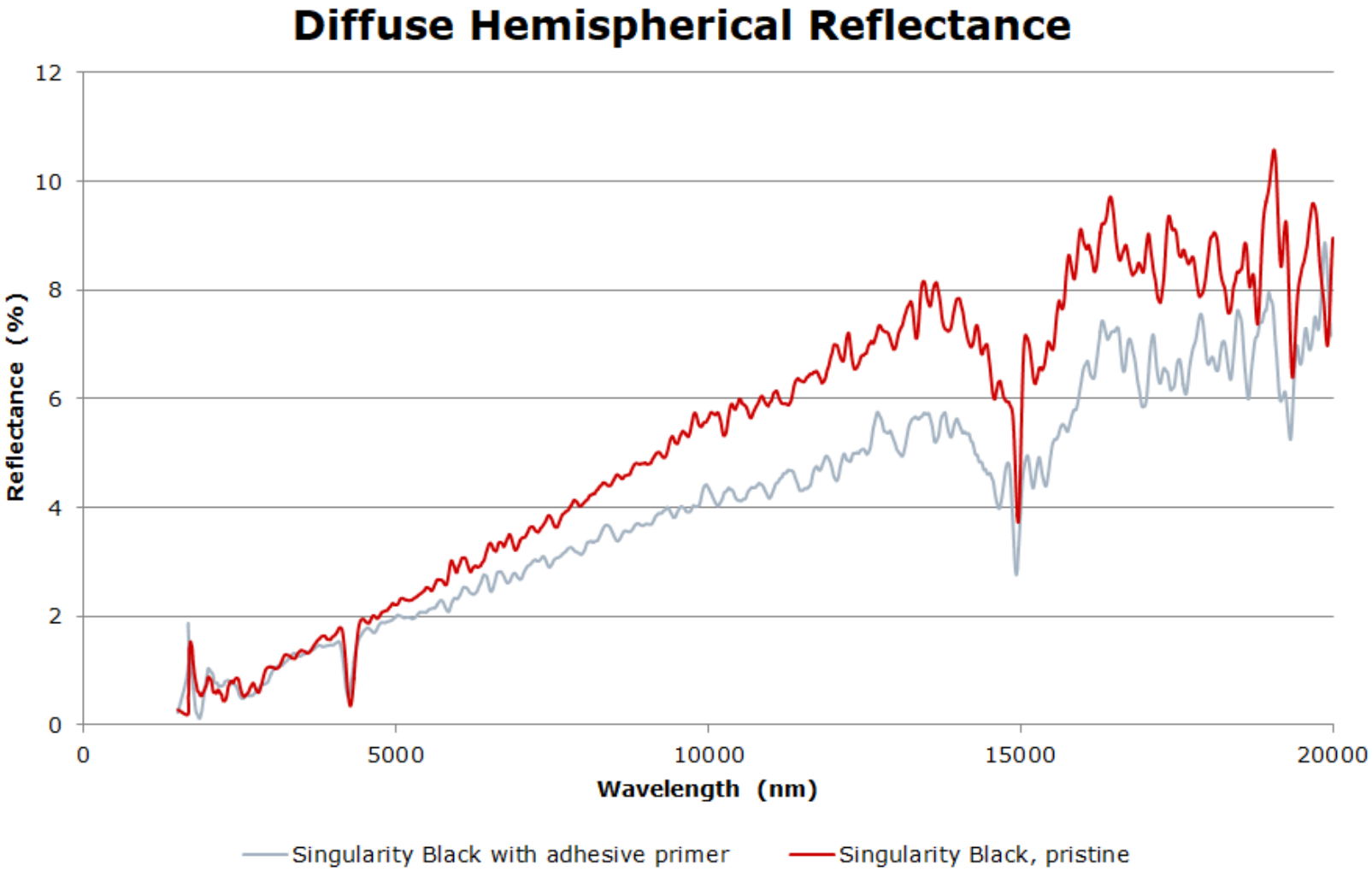
DRIFTS

We needed a rapid method to grade the coatings in the IR. Our FTIR system, equipped with a diffuse reflectance accessory (Pike EasiDiff) gives us a way to compare the relative reflectance of our nanotube arrays.

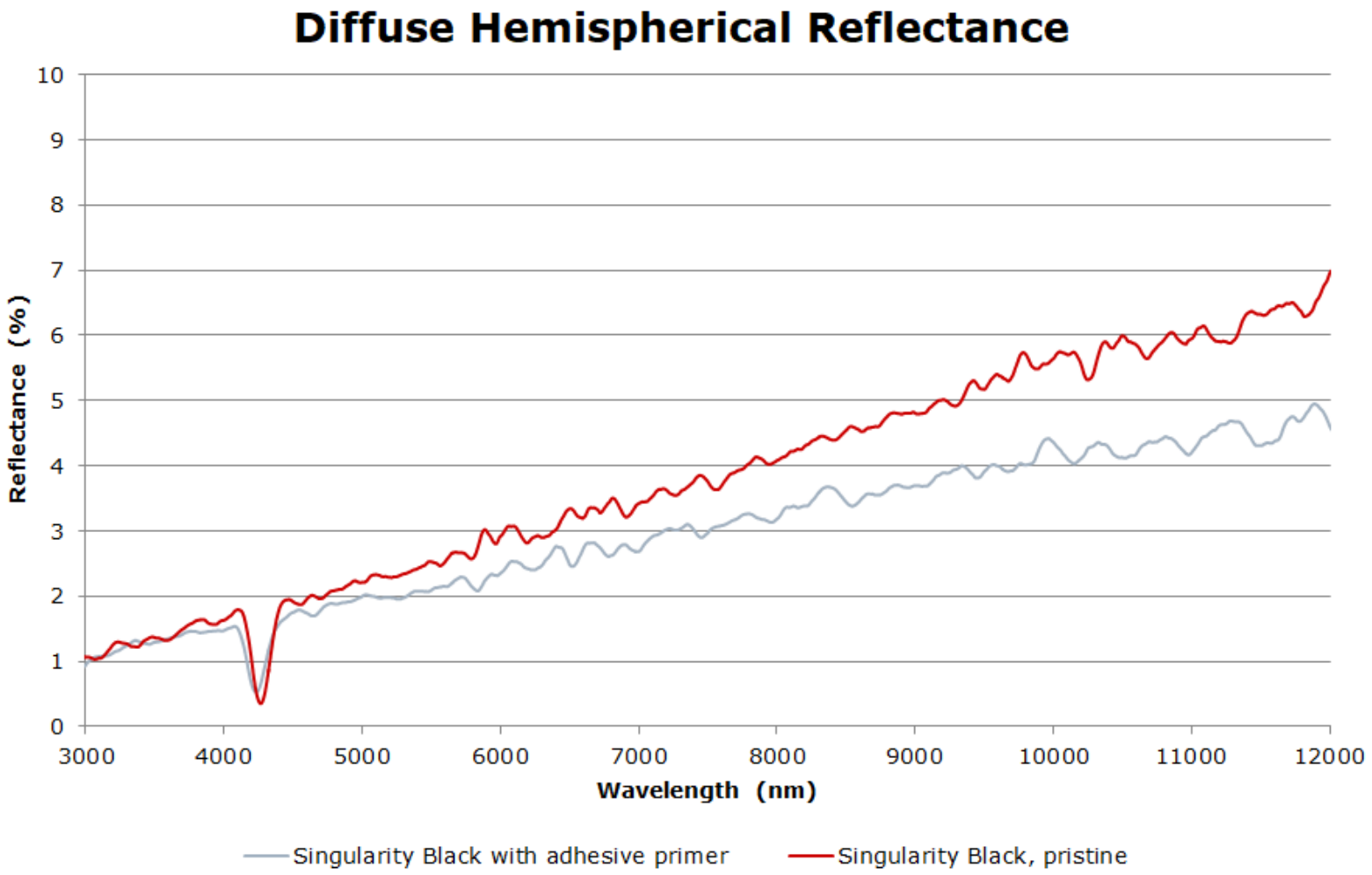
- We measure:
  1. Reflected energy spectrum from 2.5-25 microns
  2. Beam Energy (BE) which is a rough average across the range.
     - A mirror gives a BE ~6000
     - Krylon flat black on mica, BE = 324
     - Our best arrays, BE= 2



MWIR-LWIR Diffuse Reflectance

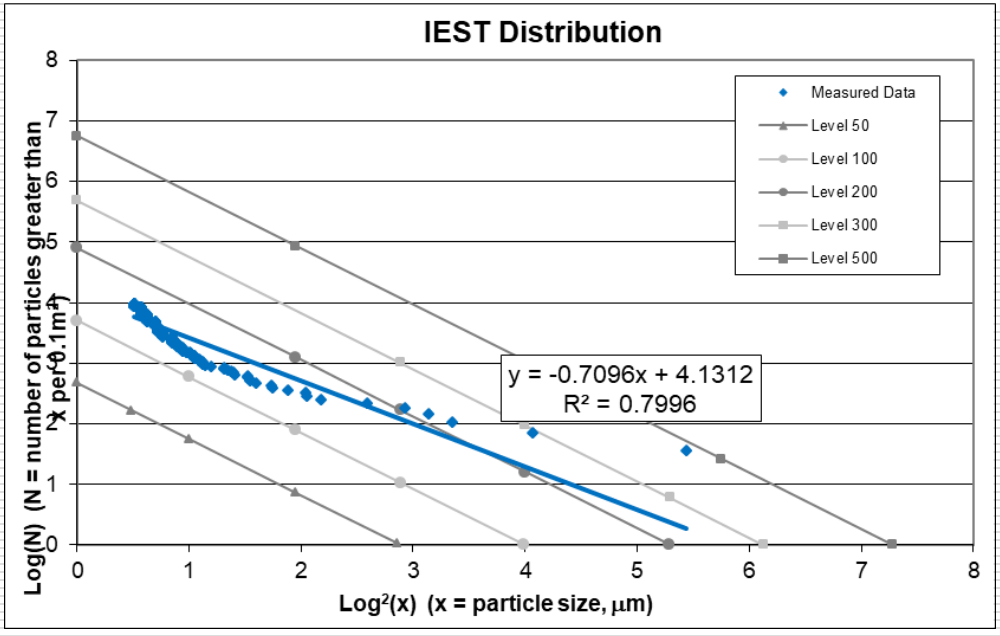


Singularity DRIFTS data

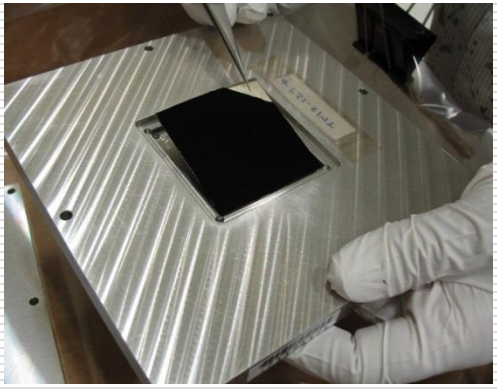


Thermal characterization

- Thermal Cycling
  - Singularity samples were thermal cycled 3X from-60°C to 85 °C at 10-20 °C/min, 30 min soaks, N2. No changes were observed.
- Outgassing
  - 24 hr at 100°C, with a Thermal Quartz Crystal Microbalance (TQCM). The rate was 3.95×10^{-15} g/cm^2-sec, similar to metals.
- Emissivity & Absorbtivity e=0.99, a=0.86 by AZ TEMP 2000A
- Vibe
  - GEVS II and Delta IV tests- passed
- Cleanliness
  - IEST-STD-CC1246 Particle Level ,Clemex particle sizer



Vibration Level	GEVS		BPL	
Axis	X	Z	Z	X
Percent area covered (PAC) ($\times 10^{-3}$)	2.86	1.19	1.19	25.3
IEST-CC-1246 Level	100	148	248	300



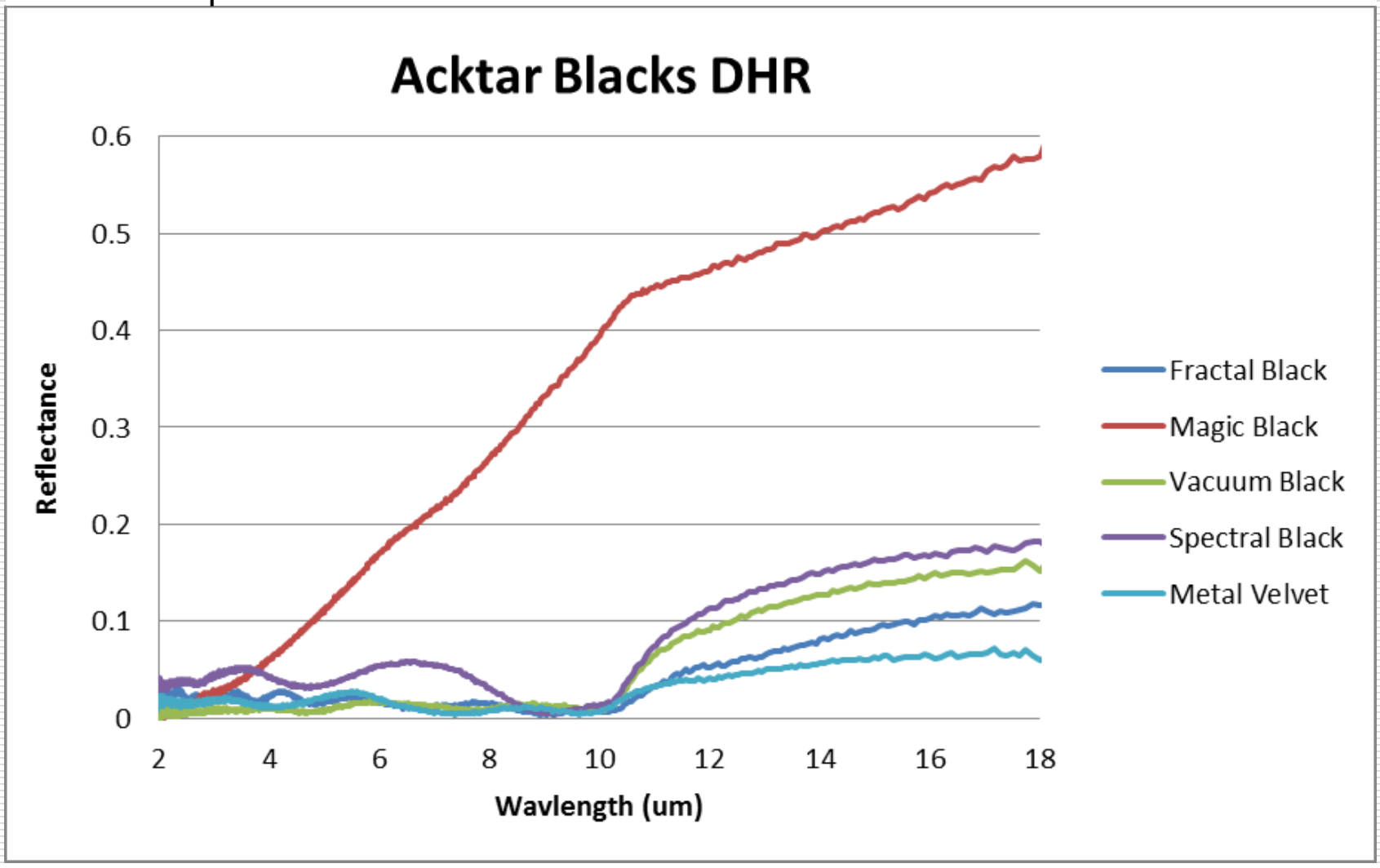
Summary of Singularity Black

- Singularity Black has low diffuse/specular reflectance in the broadband
  - SWIR: 1.25 – 1.75%
  - MWIR: 1.0 – 2.0%
  - LWIR: 2.0 – 4.5%
  - FIR (<50 μm): < 10%
- Thermally stable up to 300°C
- Mechanically stable to rocket-type vibrations, adhesive primer improves abrasion resistance to withstand incidental contact
- Processing conditions are amenable to aluminum and copper parts
- Applicable via spray-coating, dip-coating, and brush-coating

Questions?

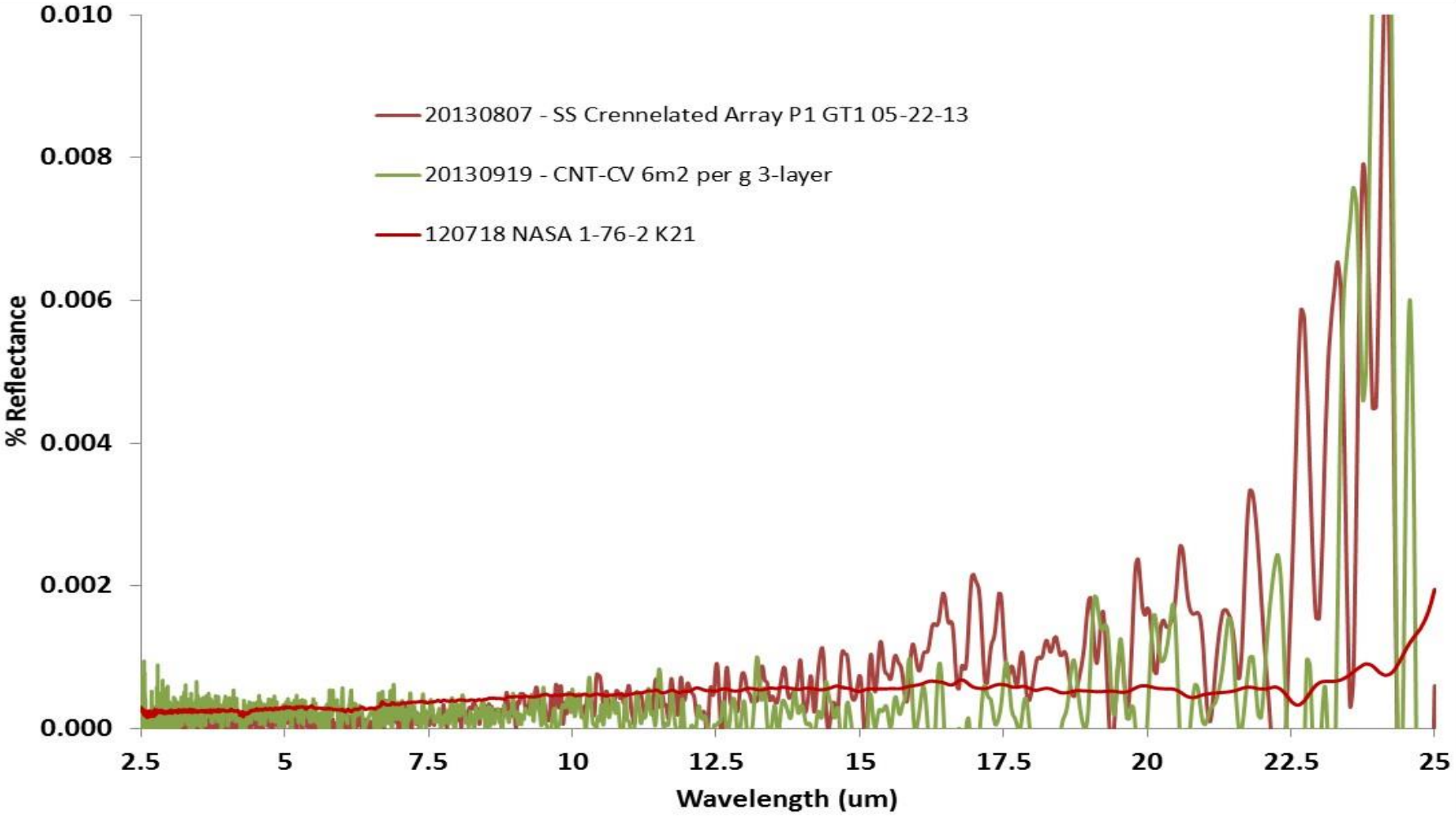
Acktar DHR spectra

- Compilation of directional hemispherical reflectance spectra of Acktar Black products



DRIFTS

- Three avenues for array growth give consist IR spectra, with 99.99+ absorbtion past 20μm



Top Performers- DRIFTS