Nanostructured Optical Black Coatings

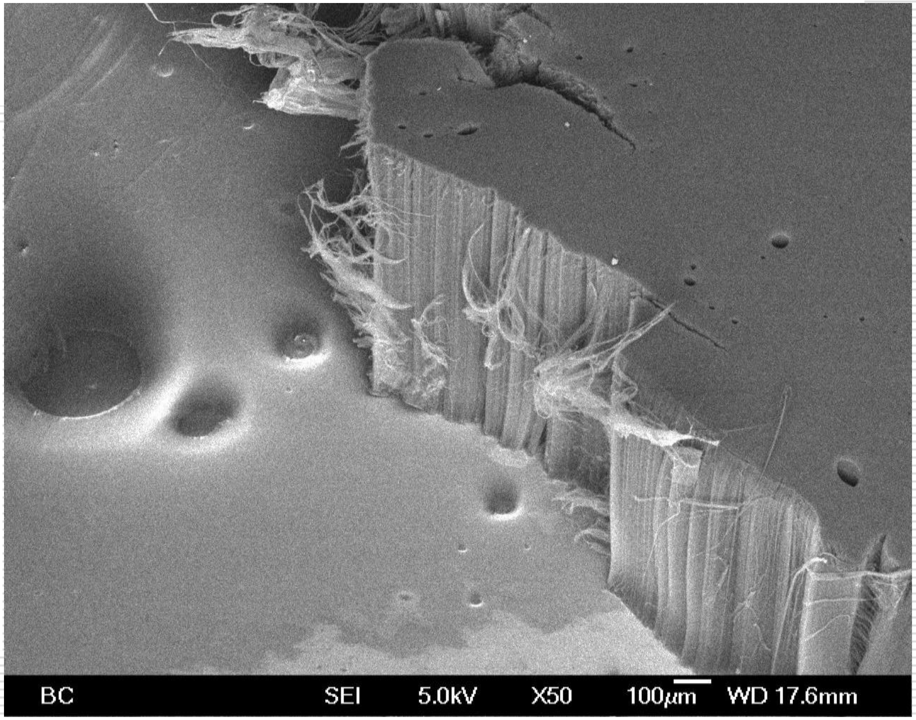
NASA SBIR Phase II Contract NNX13CP46C

PI: David Carnahan
NanoLab, Inc.
179 Bear Hill Rd.
Waltham, MA 02451
dcarnahan@nano-lab.com
Phone 781 609 2722

Sub: Beth Kelsic
Ball Aerospace
1600 Commerce St
Boulder, CO 80301
bkelsic@ball.com

Update for 2014, S2.02

Mission:
NanoLab offers product and process development services for nanoscale sensors, devices, and nanotechnology-enhanced coatings & composites.
We serve customers at all technology readiness levels, from basic research through prototyping, optimization, and testing, to product manufacture.



Capabilities

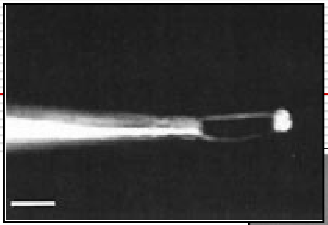
- Nanomaterial Synthesis
  - Air-free chemical synthesis
  - Hydrothermal synthesis
  - Full wet chemical lab
  - CVD reactors
  - In-house CNT production & functionalization
  - Plasma & ozone etching
  - Electrochemical deposition
  - Access to:
    - E-beam lithography
    - Full clean room
    - 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 & Paste Formulation Tools
  - Ultrasonic dispersion equipment
  - Screen & inkjet printers, and drop-on-demand printing

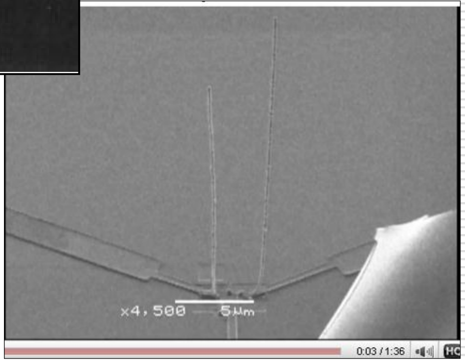
- Characterization
  - Optical
    - FTIR
    - UV-VIS-NIR
    - Raman
  - Thermo-physical
    - TGA
    - DSC
    - DTA
  - Mechanical
    - Tensile
    - Impact
    - Adhesion
  - Electrical
    - Resistance
    - Impedance
    - Capacitance
    - Inductance

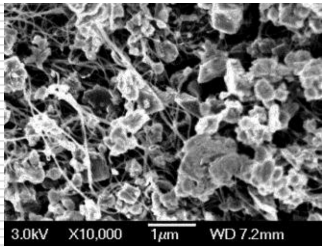
Material systems: carbon nanotubes, nanoparticles & nanowires of oxides, metals, carbides
Matrices: epoxies, silicones, rubbers, urethanes, polyimides, metals, carbides, oxides

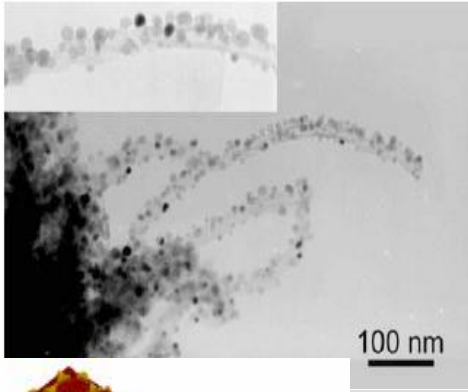
Partial Project portfolio

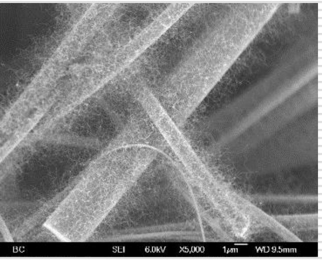


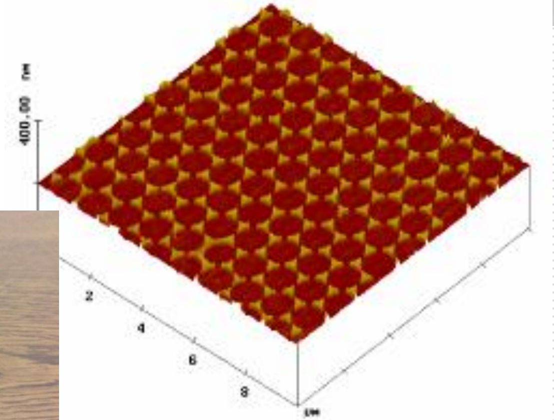
- Nanoscale tweezers/grasping tools
- Catalytic nanoparticle coatings (DOE)
- High Emissivity, optical black coatings (NASA)
- Scintillator coatings (Zeiss)
- Radiation sensors (Private)
- E-beam & nanoscale lithography services
- Toughened B_4C armor nanocomposites (Army)
- Wearable elastomeric strain sensors (Adidas)
- Corrosion resistant coatings & primers (Navy)
- CNT-reinforced epoxy composites (Schlumberger)
- Wear indicating sensors for bearings (Navy, NHBB)
- Graphene system design & automation (AMU)
- Medical gas sensors (Private)
- Endotracheal tube position sensor (Miach)
- Filtration media for virus removal (Lydall)
- Nanoparticle based transfection (BioRad)

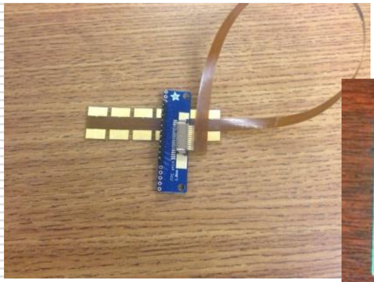


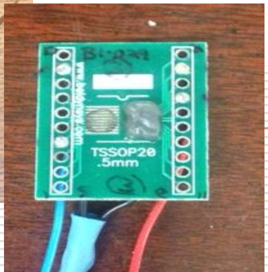






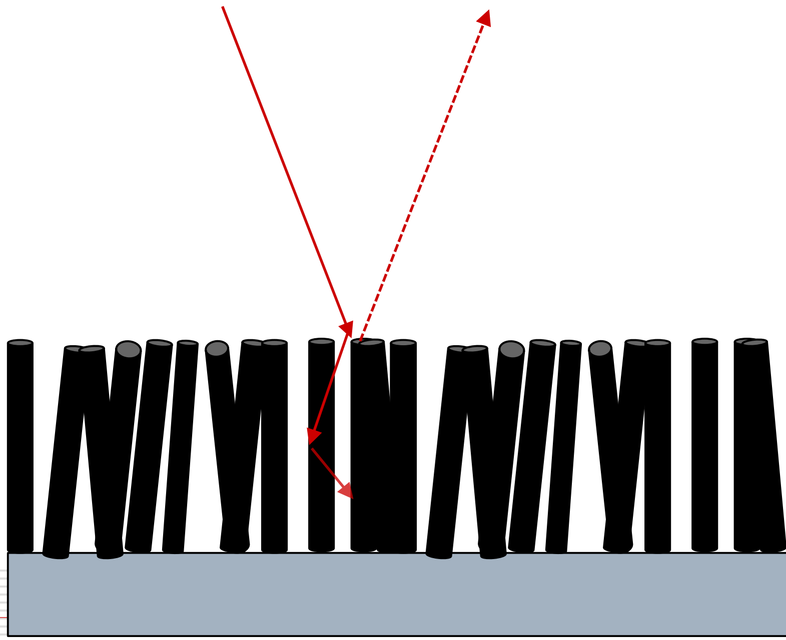


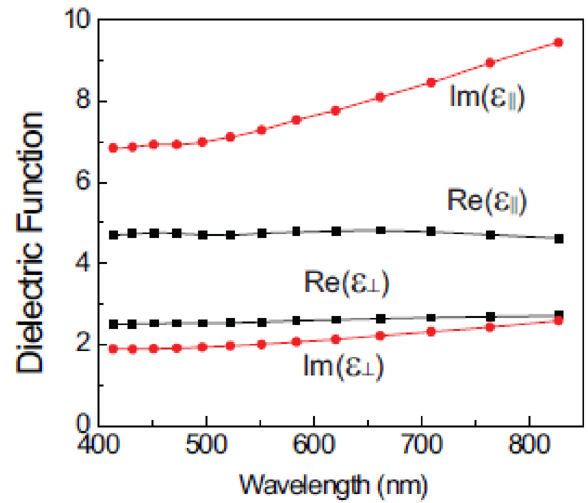




How do we make a good black surface?

- **Minimize Reflection**: Coating must be a near index match to the atmosphere above it. We do that with a sparse, low volumetric density (~5vol%) CNT coating.
- Provide **long total path length** for absorption. A coating should be multiple wavelengths thick at the wavelengths we care about. CNT are sub-λ in diameter, & supra-λ in length.
- Provide **short path length for interactions**. Spacing between CNT can be sub-λ
- Inelastic (**lossy** iteractions) with the nanotubes.



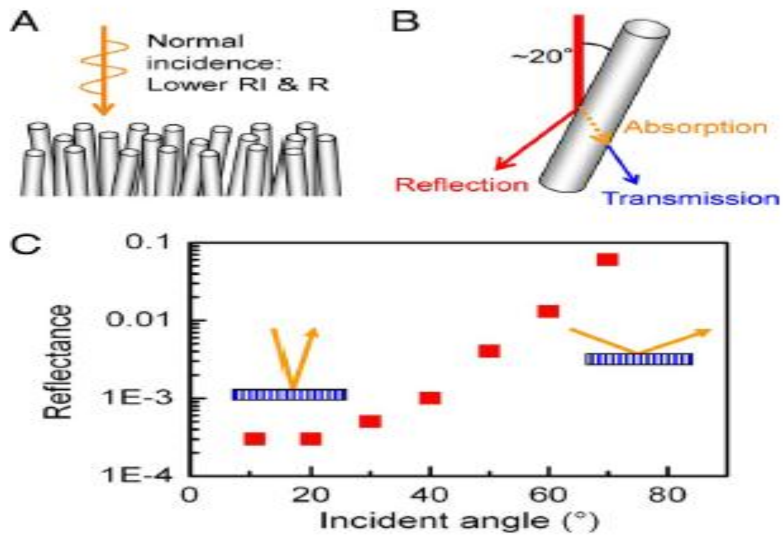


Hua-Bao, Xiu Lin Ran, Timothy Fisher, "Optical properties of vertical arrays of multiwalled carbon nanotubes from FTDT simulations" 15 March 2010 / Vol. 18, No. 6 / OPTICS EXPRESS 6353

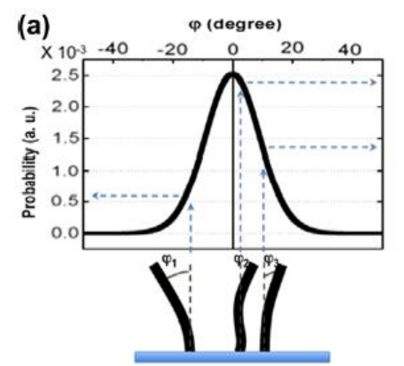
Phase II Technical Objectives

1. Correlate the optical properties of nanotube arrays to their growth parameters; determining the influence of:

   diameter
   site density
   alignment
   length
   graphitization



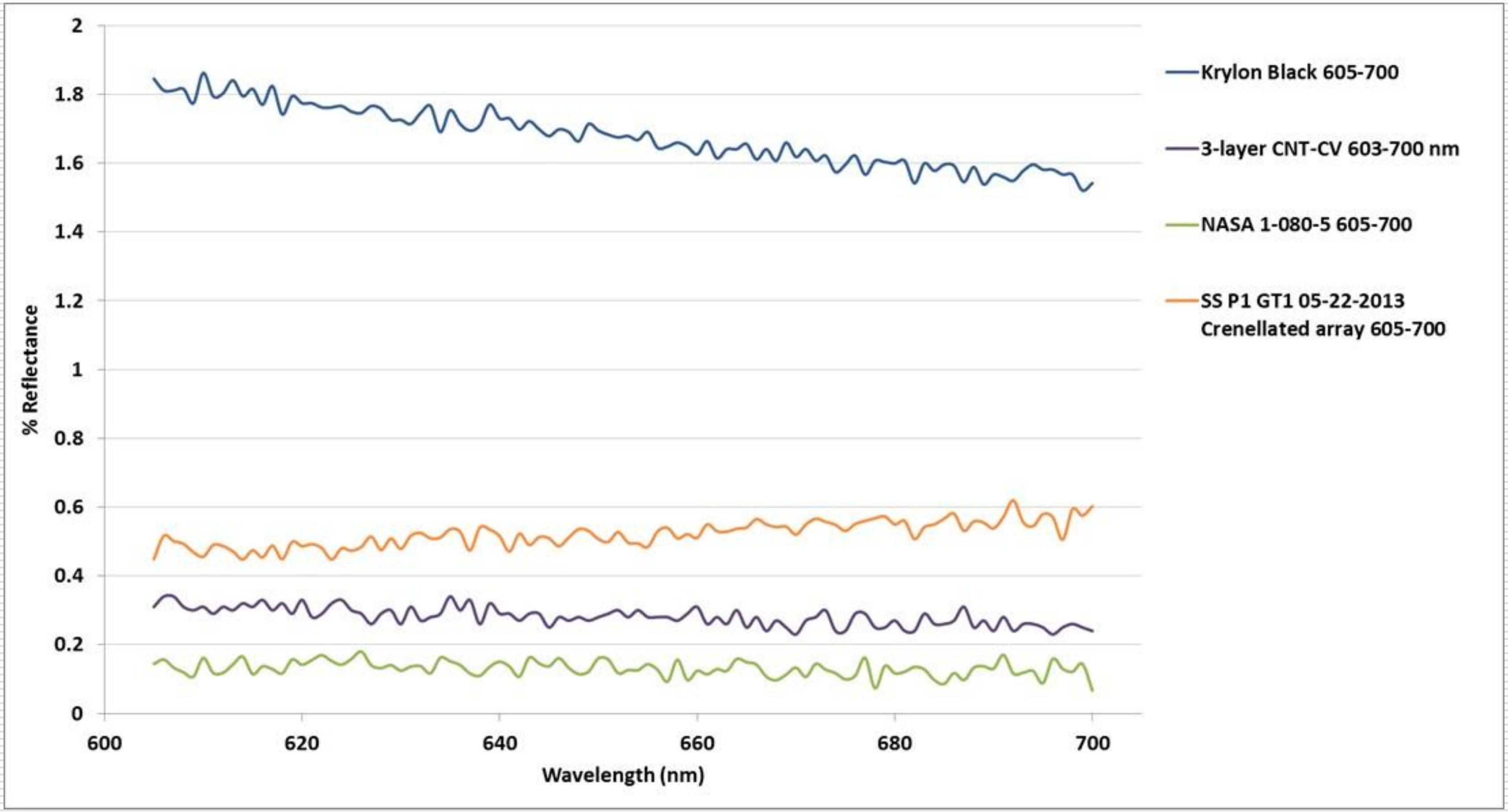
2. Develop adhesion and scratch resistant treatments.
3. Scale processes for on flexible substrates. (Titanium, Stainless steel, mica, etc.)
4. Develop processes for complex 3D parts



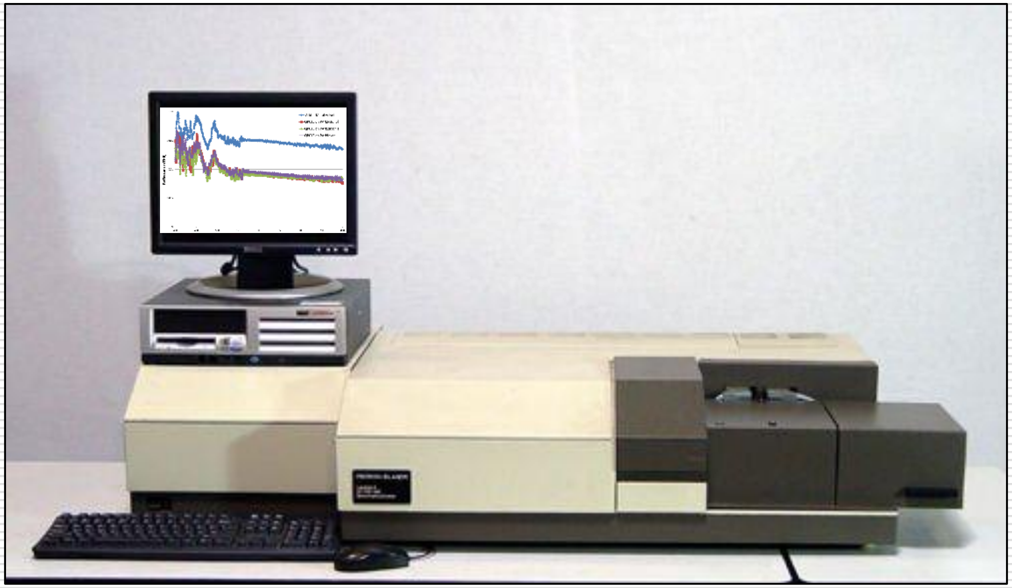
Ref: Mizuno PNAS, 2009, 106, 15
Enhanced optical absorption cross-section characteristics of multi-wall carbon nanotubes, C. Ni, P.R. Bandaru, Carbon 47 (2009) 2898 –2903

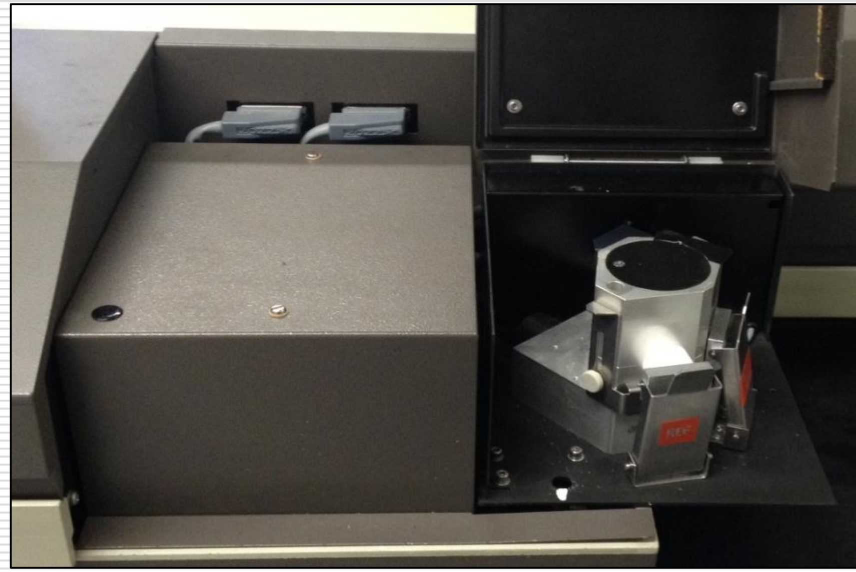
UV-Vis Data

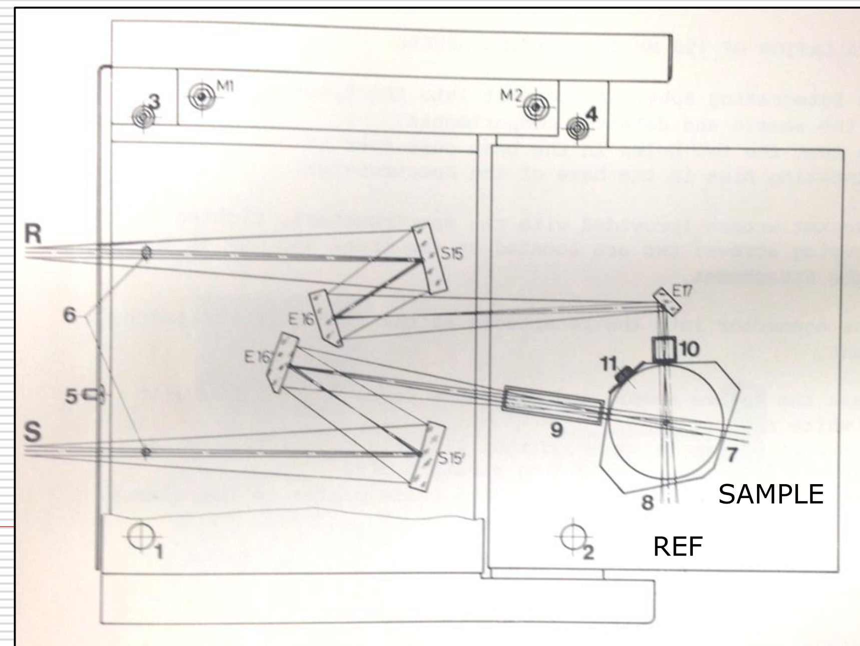
- Best performers are 0.1% THR in the optical.



Perkin Elmer UV-VIS w/60mm integrating sphere







UV-VIS-NIR Measurement
THR- Both Diffuse and Specular reflection
Wavelengths from 280nm to 2500nm

Questions for 2013-2014

1. Over the last year, we asked some new questions.

    1. Could we develop a catalyst that can be spray deposited and allow growth on nearly any surface?

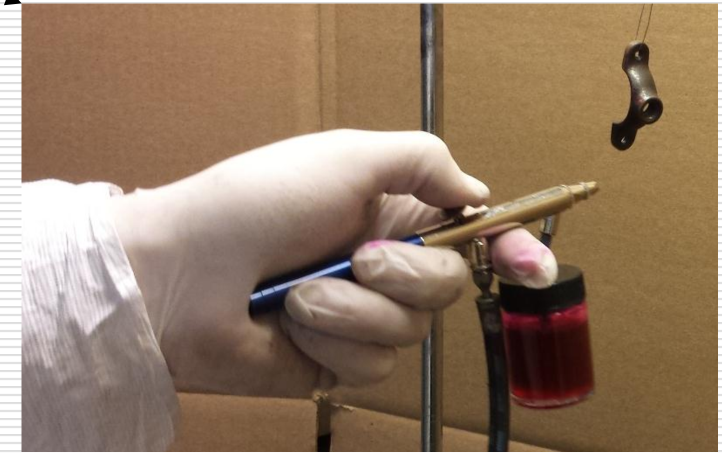
    2. Can we achieve the same performance without having to grow the CNT in-situ… perhaps with a sprayable or paintable formulation?

       Can it be as black across optical wavelengths?

       Could it adhere as well or better than our arrays?

Substrate Catalyzation

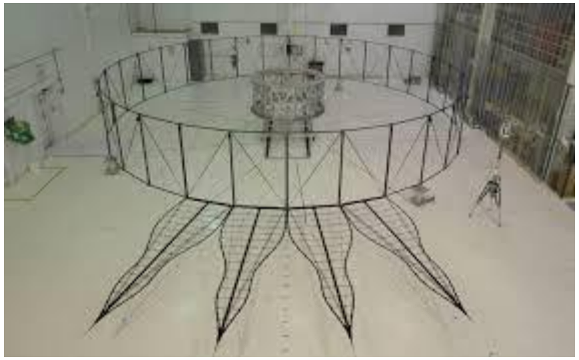
- 2013 catalysis Al2O3 +Fe:
  - Cleanroom
    - Sputtering
    - Evaporation
      - 10$/m^2 at large volumes
- 2014 Catalysis with sol-gel
  - Spray-coating
    - <$2/m^2 at volume
  - Knife / Roll coating
  - Spin Coating

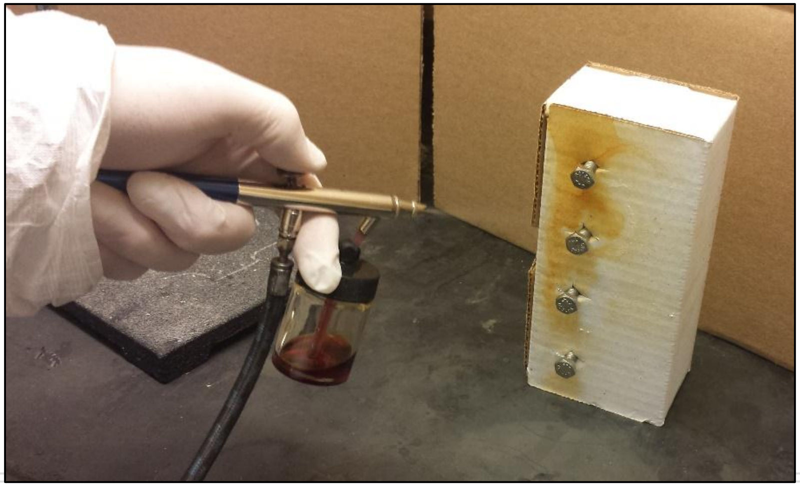


Substrates: SS sheet, Ti sheet, mica sheet, carbon veil, complex parts

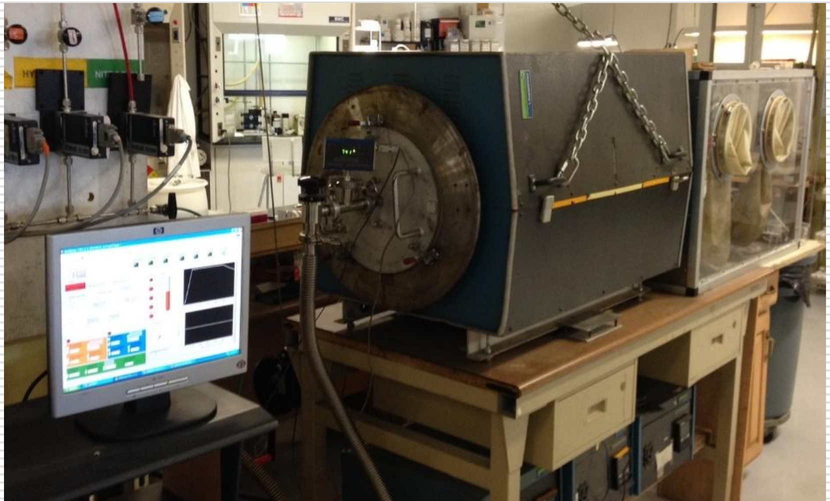
Sprayable wet catalysts for CNT optical black coating

- We wanted a one-step process for catalysis that would make aligned arrays with good optical performance.
  - We developed an iron-alumina sol-gel formulation that could be applied to complex shapes.
  - Spray offers significant cost reduction
    - 1/5 of prior process in $\$/m^2$
    - Actually scalable to m^2
    - Complex parts
  - Growth process proceeds as before…CVD conditions



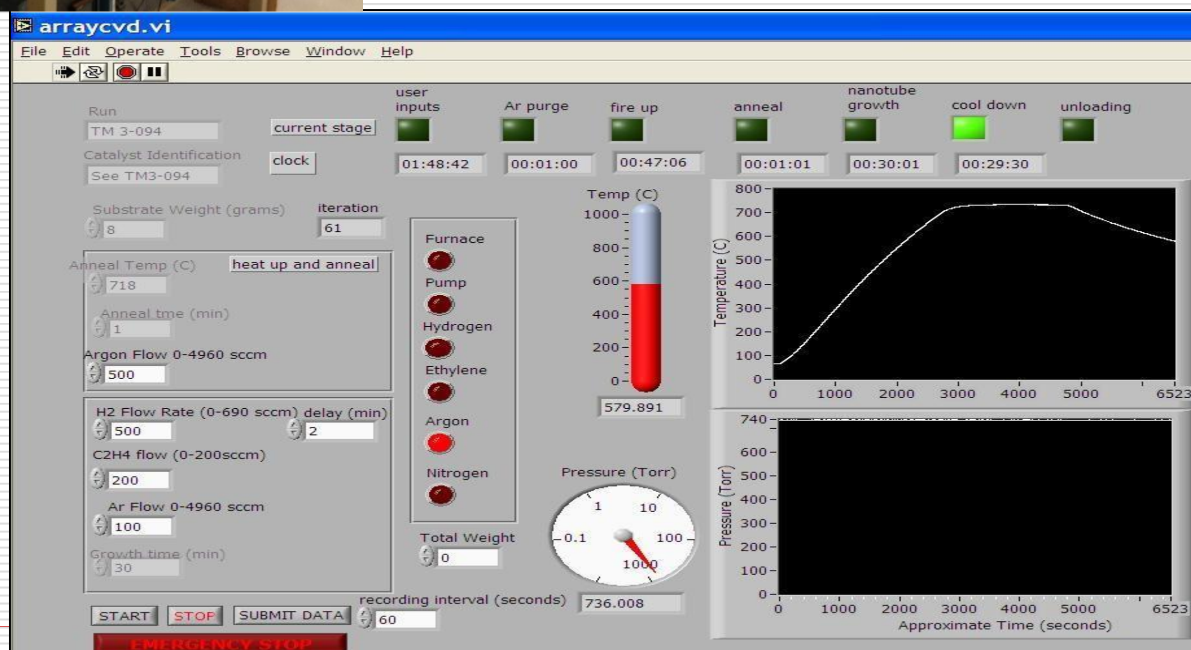


CVD Deposition of VANTA Black Coating



- Furnace accepts parts 10” dia x 24 long
- MKS mass flow controllers
  - Ar, H_2, C_2H_4
- Automated with LabView

7 Step Program
1. Insert
2. Chamber Purge
3. Heat-up
4. Anneal
5. Growth
6. Cool
7. Unload



Wet Catalyst Post CVD, Complex shapes

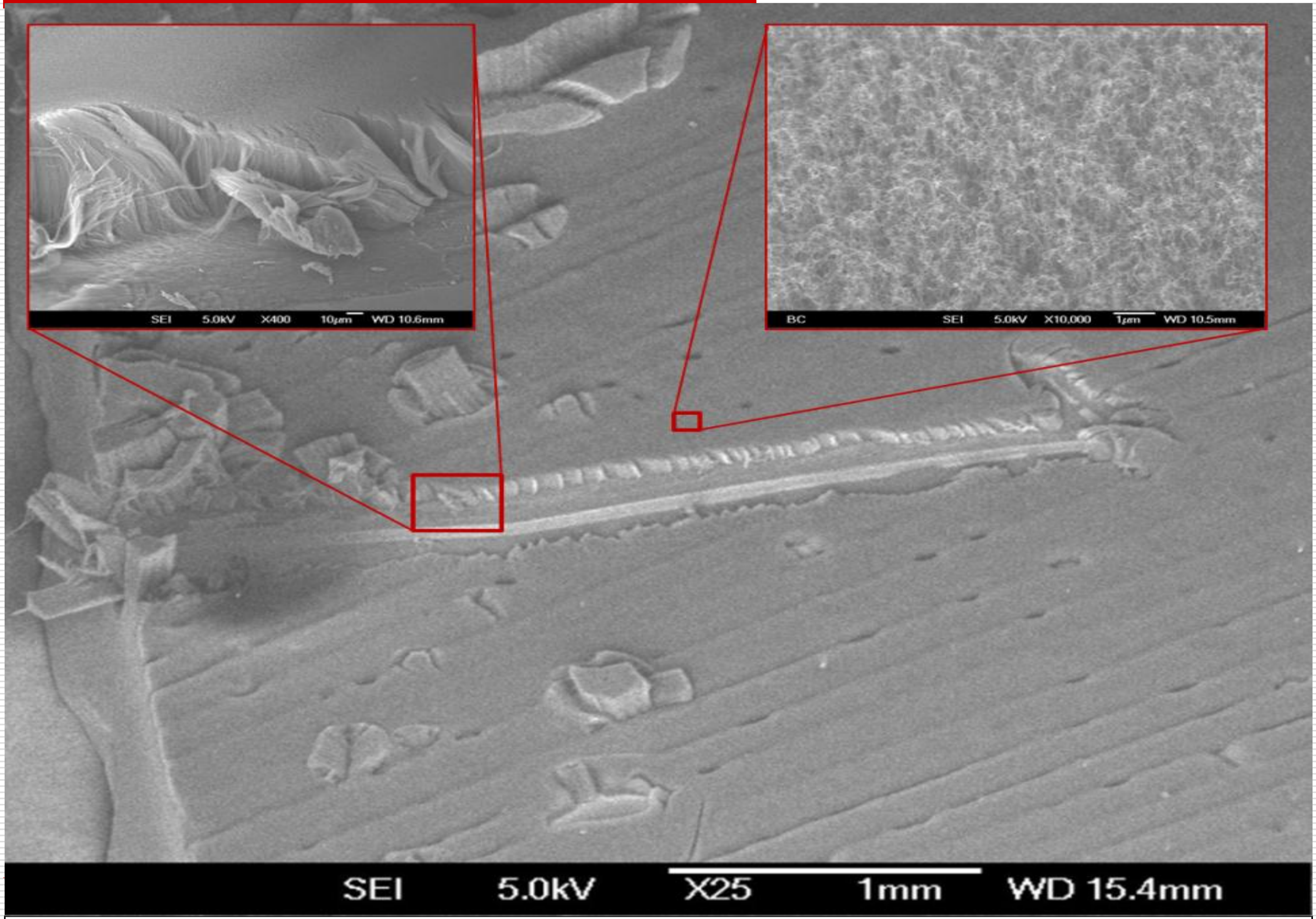
HEAD ONLY

FULL COATING

AS RECEIVED

Coating is material agnostic…vertical black coatings are produced on every substrate attempted to date…so long as they support the growth temperature.

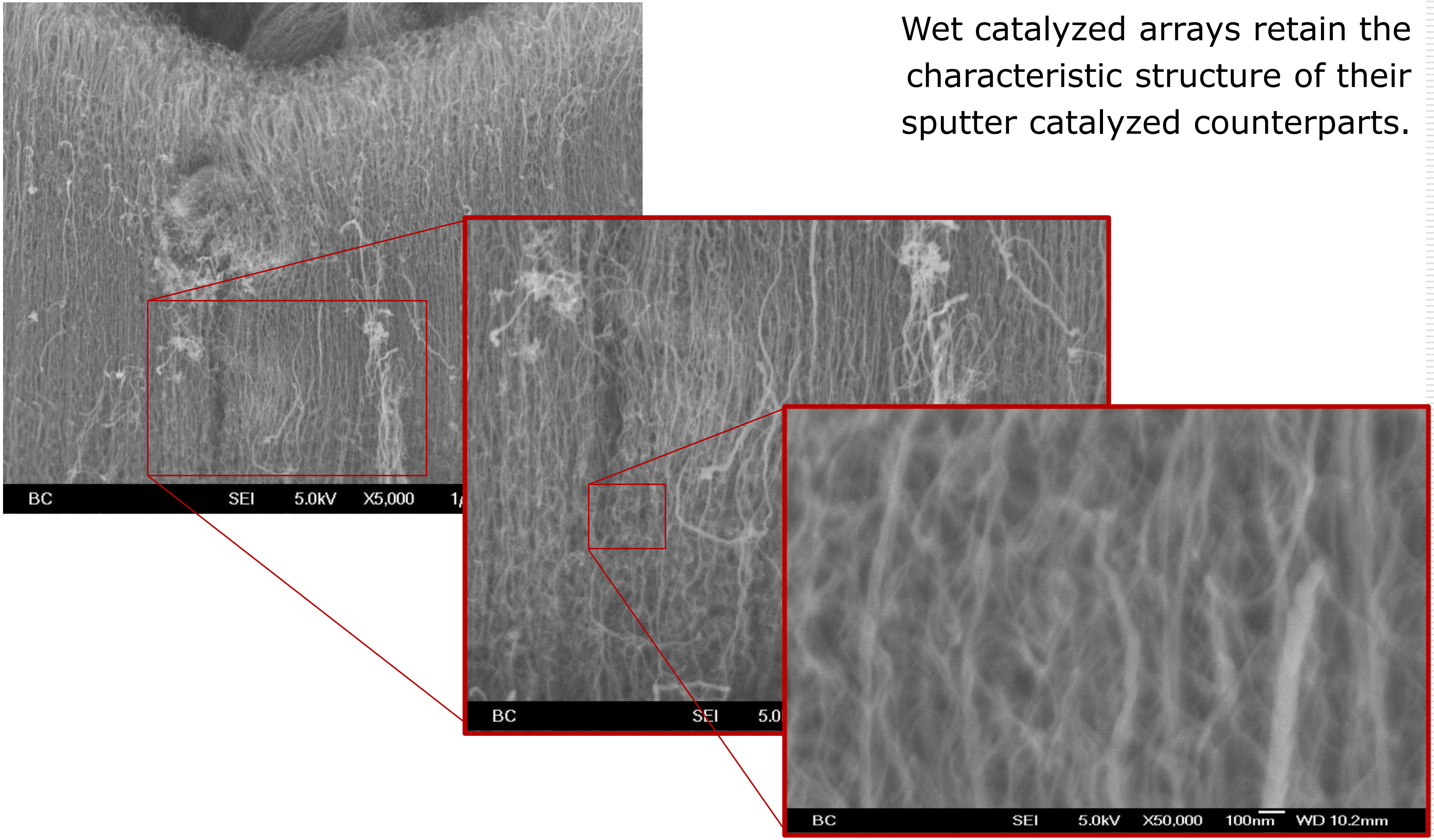
Wet catalyst results



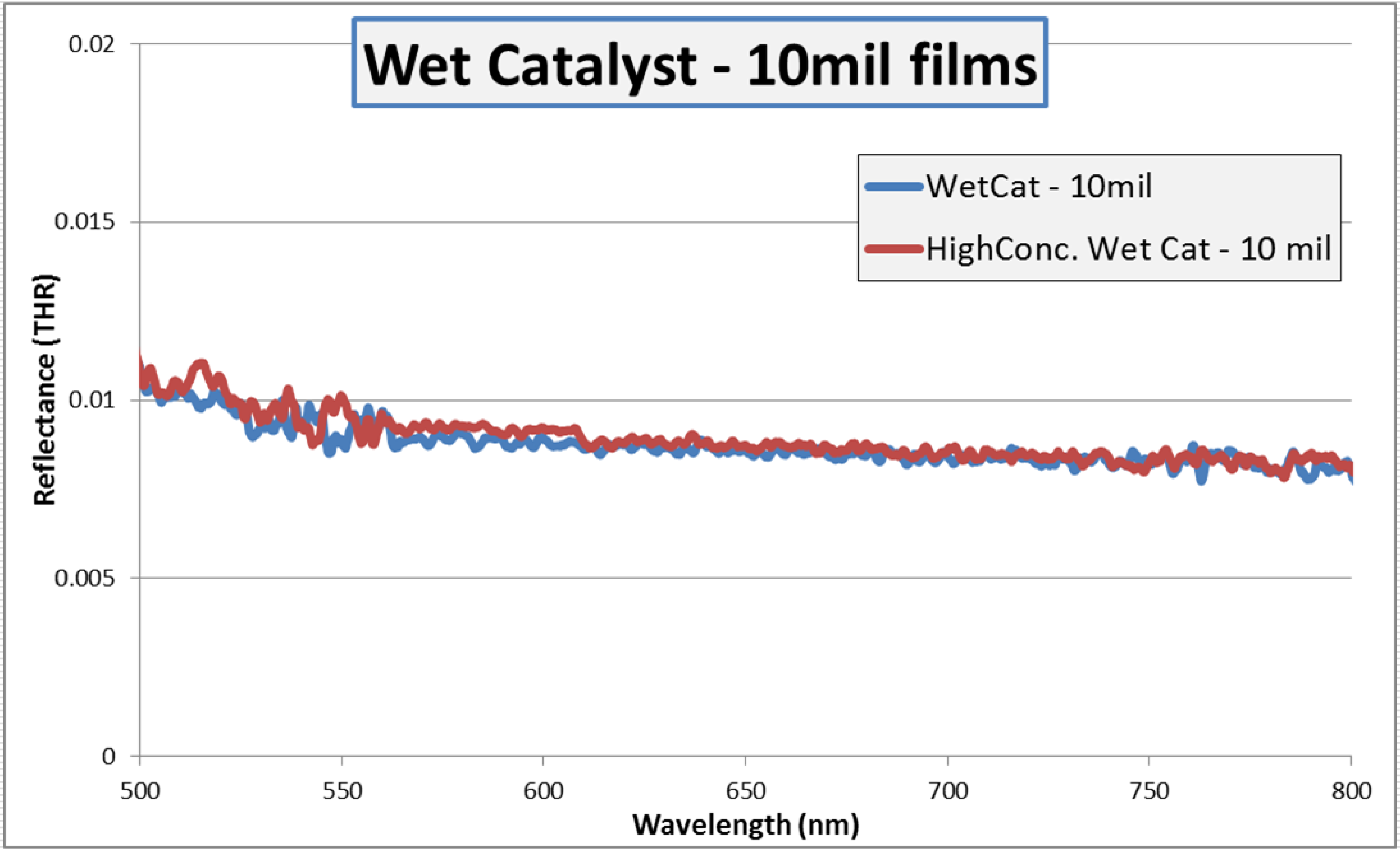
SEM of VANTA black grown from one-part liquid catalyst spin-coated onto stainless steel substrate

SEM, Wet Cat.

Wet catalyzed arrays retain the characteristic structure of their sputter catalyzed counterparts.



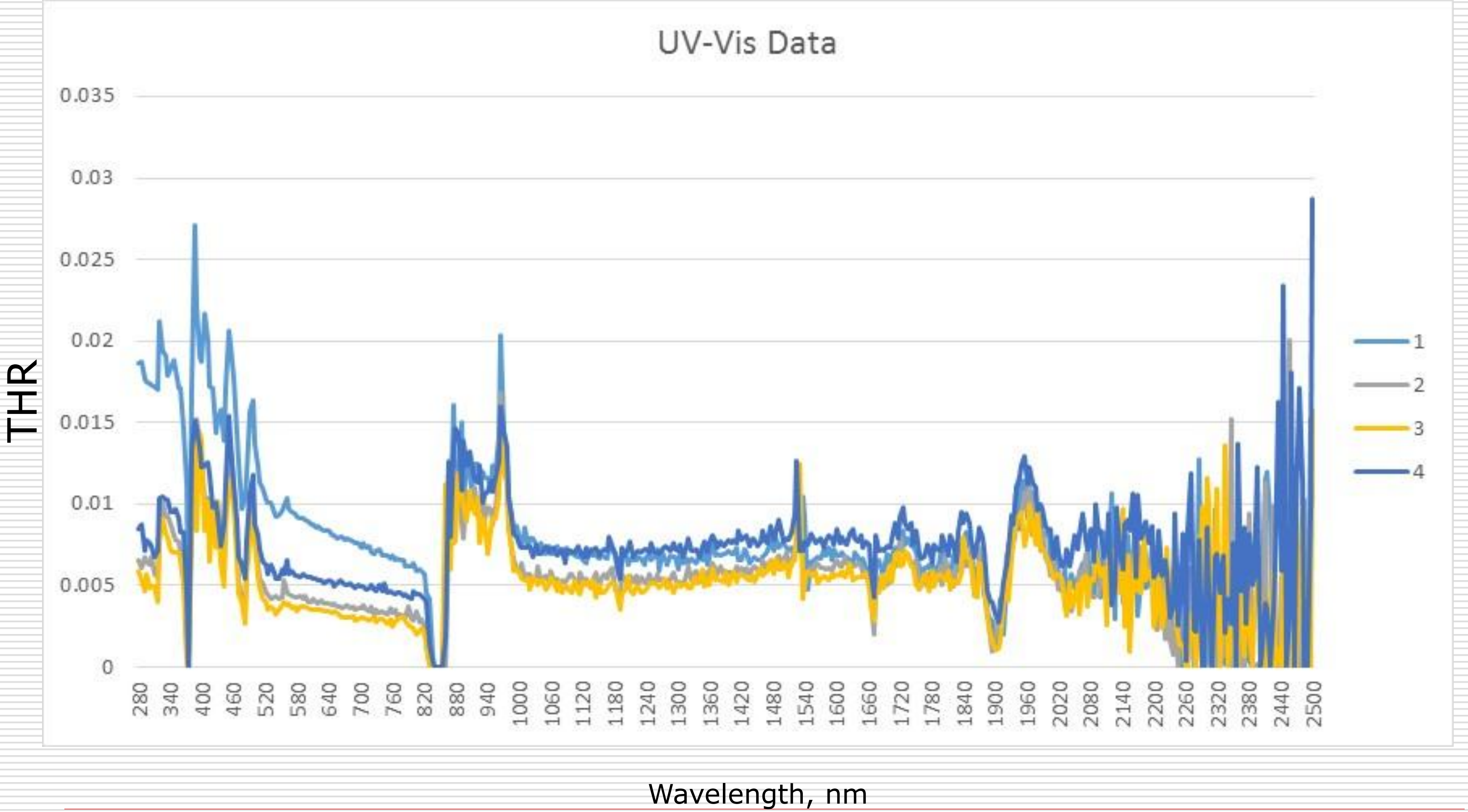
THR Optical performance of wet catalyzed blacks



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

THR from 4 types of spray catalyst formulations

- Optimization effort- iron-alumina sol-gel ratios



So what about adhesion?

A post treatment retains the black character, but makes the array nicely cohesive.

Hydrophobic?

Q2. Sprayable alternative to catalyze & grow process

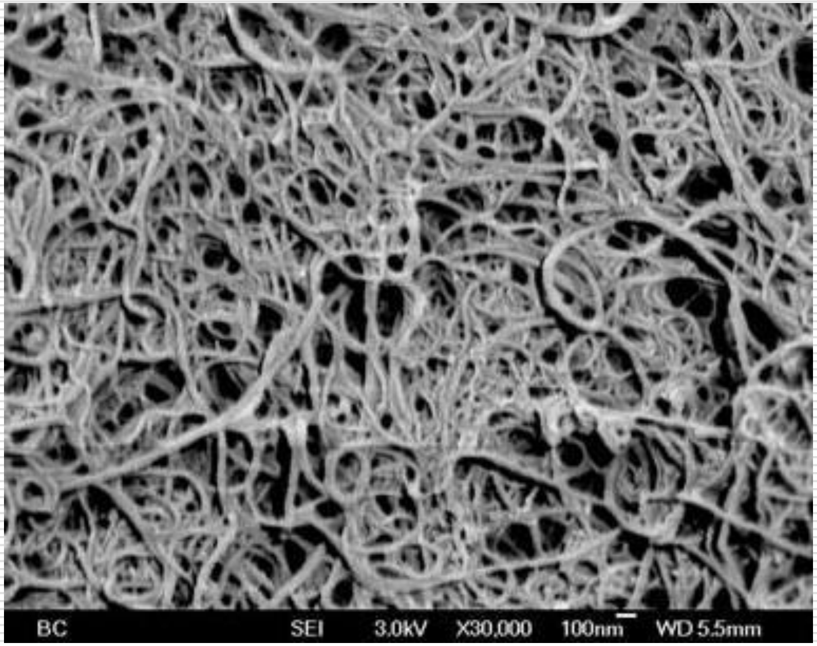
- Why do we need this?
  - Temperatures of the CVD process aren't suited to Aluminum, plastics or composites
  - We need an approach that isn't limited by furnace sizing.

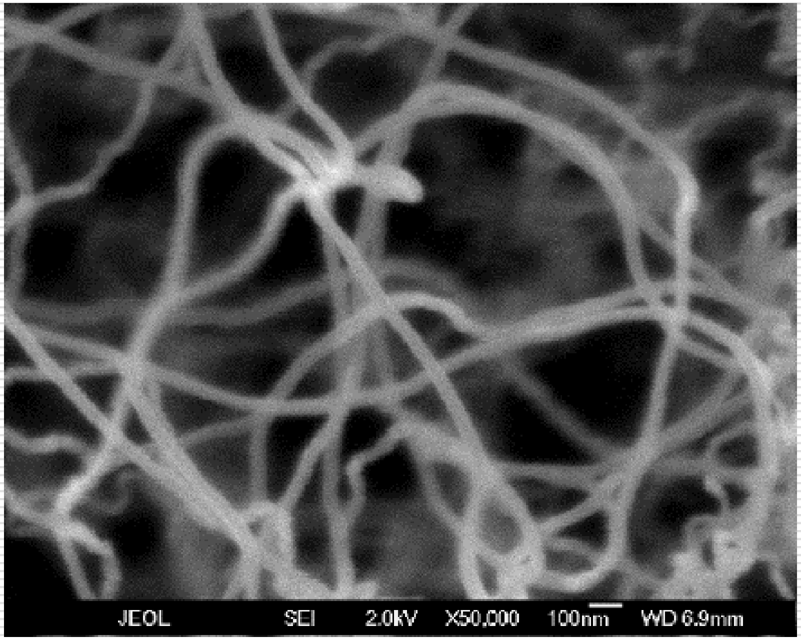
- Our challenges were:
  - How to retain the low density network?
  - How to keep any thermal processing below ~300C?
  - Can these be sufficiently black, and well adhered?
  - Could these coatings be repairable?

Sprayable formulation

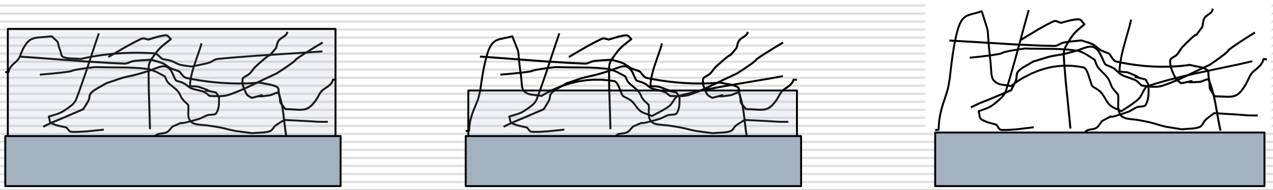
Nanotubes in a coating typically are horizontally aligned, spaghetti like, and agglomerated.

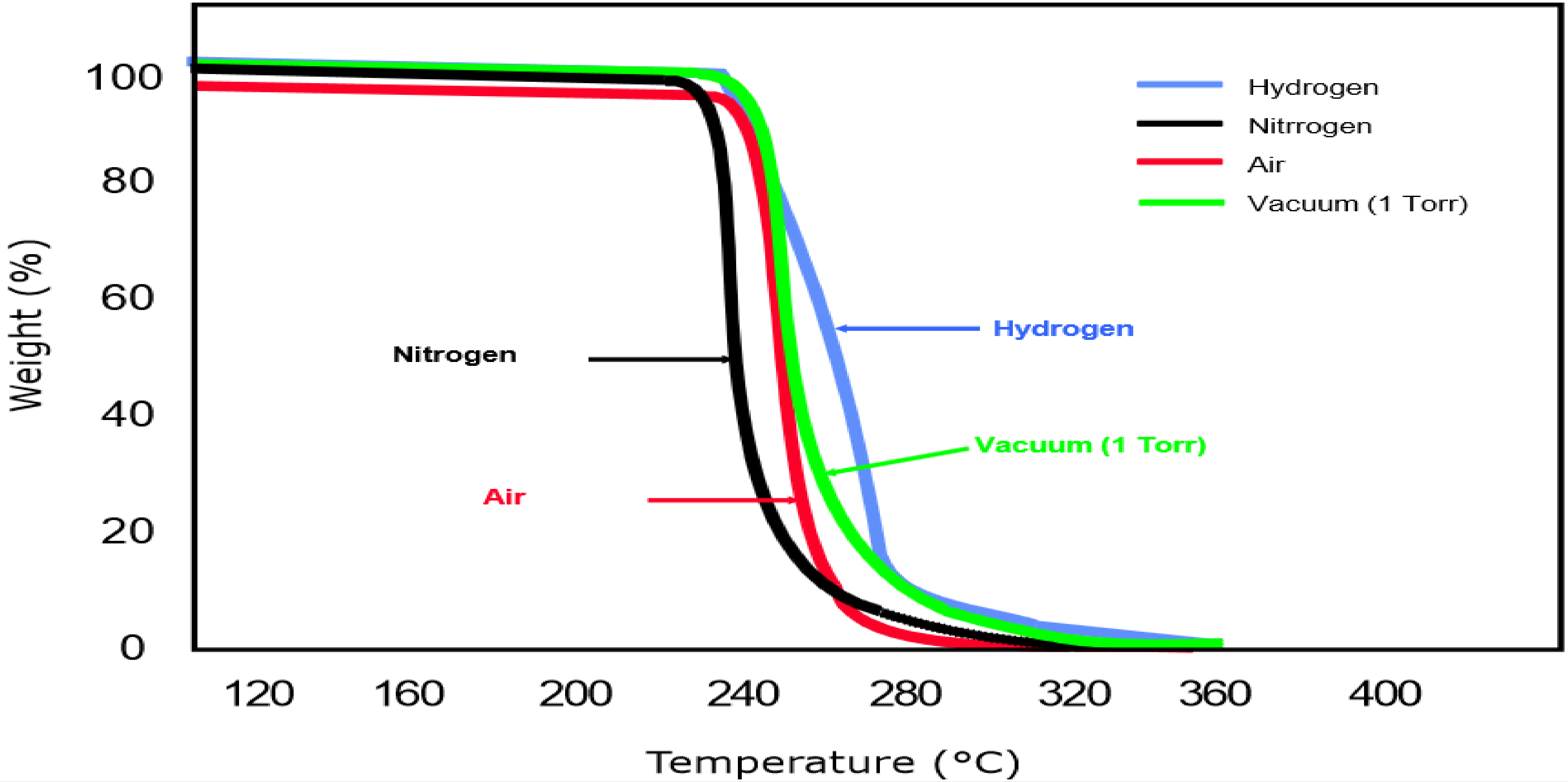
For good optical performance, we want low site density, porous networks





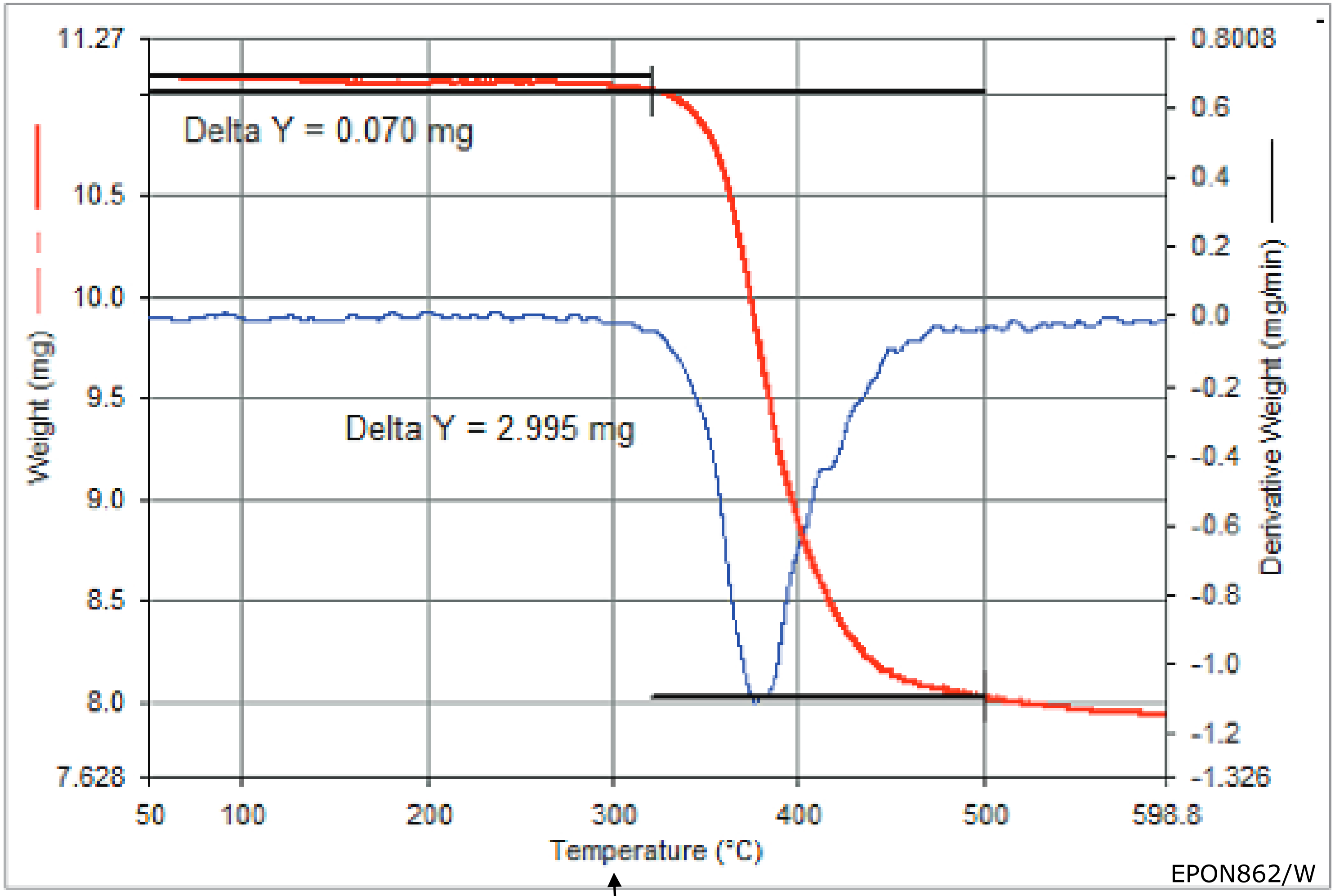
Low temperature binder phase that sublimes





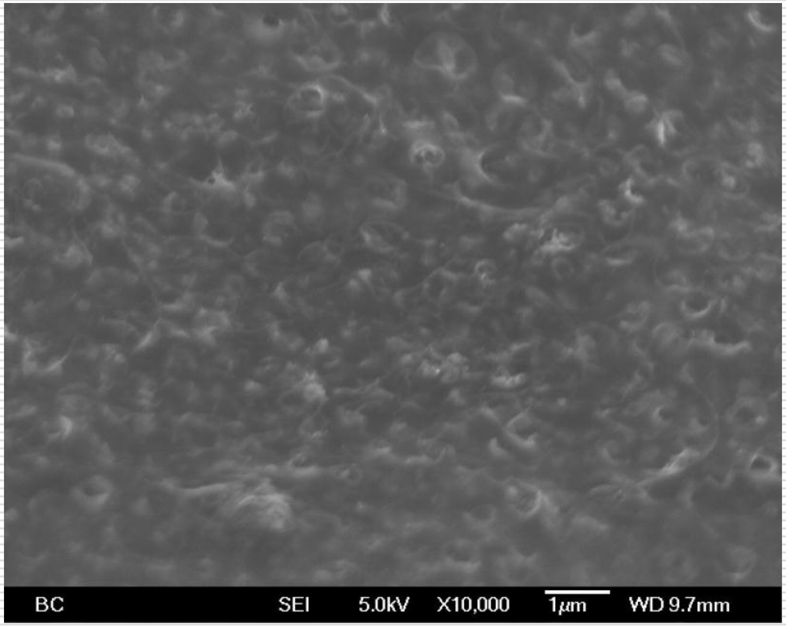
< 10 ppm residue after burn off at 300C

TGA of epoxy carbon fiber composite

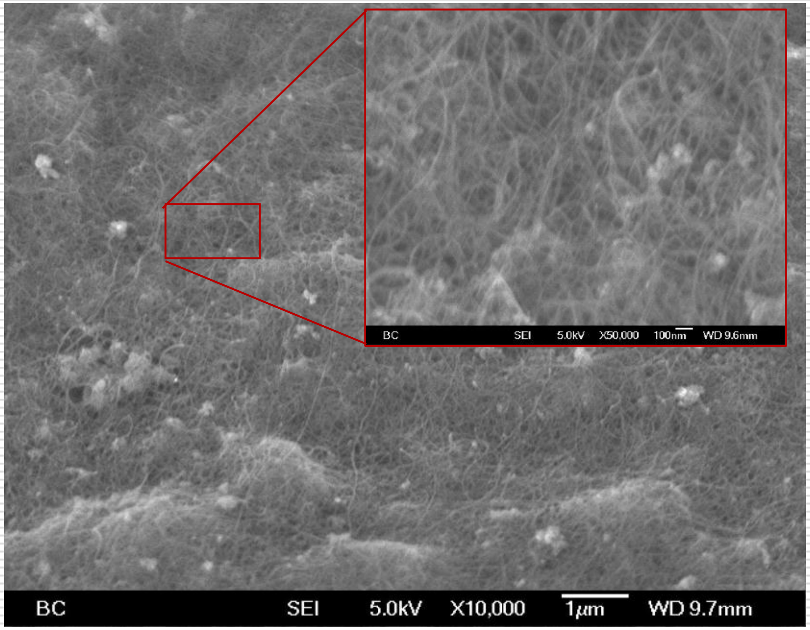


Stable to 300C

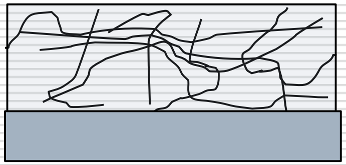
Spray-formulation pre & post burnout

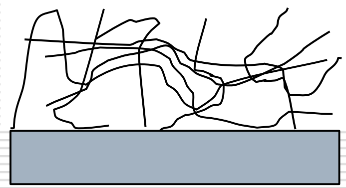


QPC15 deposited on SS foil before thermal treatment



QPC15 deposited on SS foil after thermal treatment

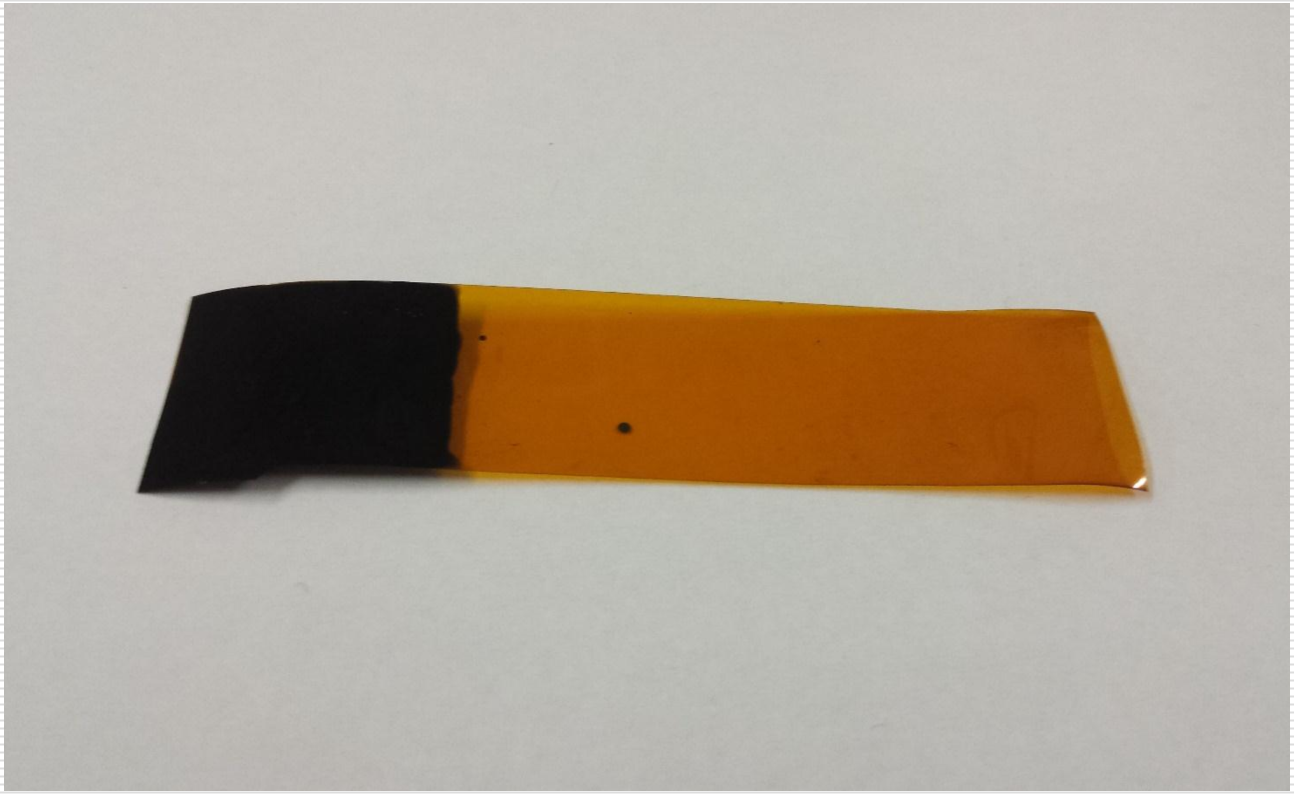




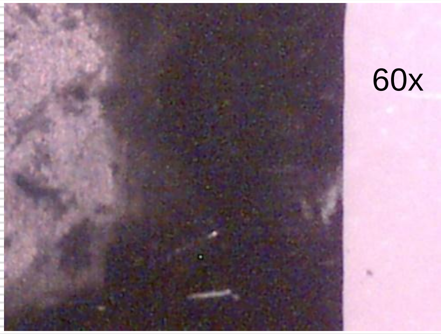
Dense, glossy grey coating due to matrix phase and density

Post 300C burnout, porosity is returned, coating becomes very black

Deposition on…



Kapton™ Polyimide



Razor Blade Edge

UV-VIS- Total Hemispherical Reflectance

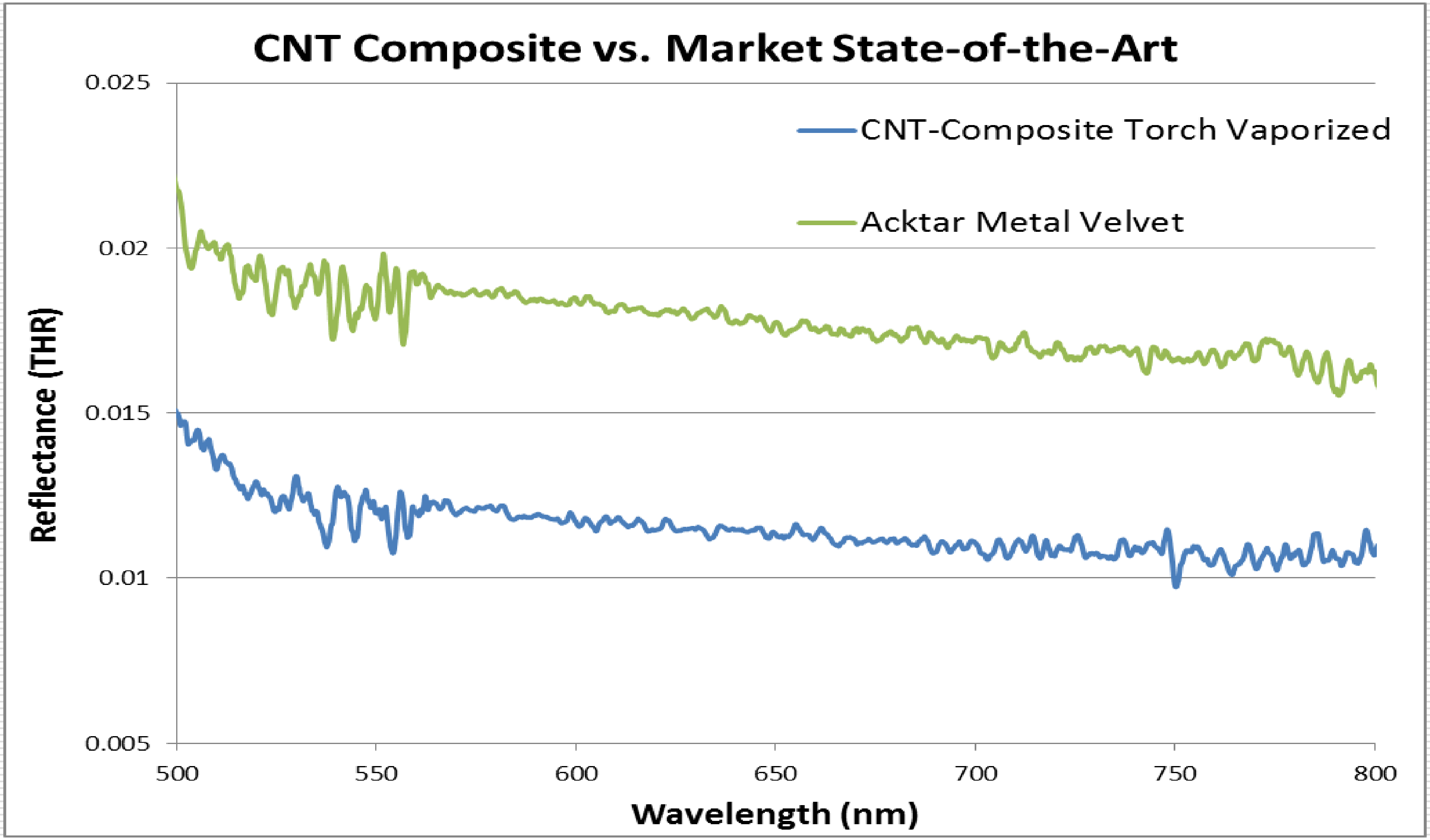
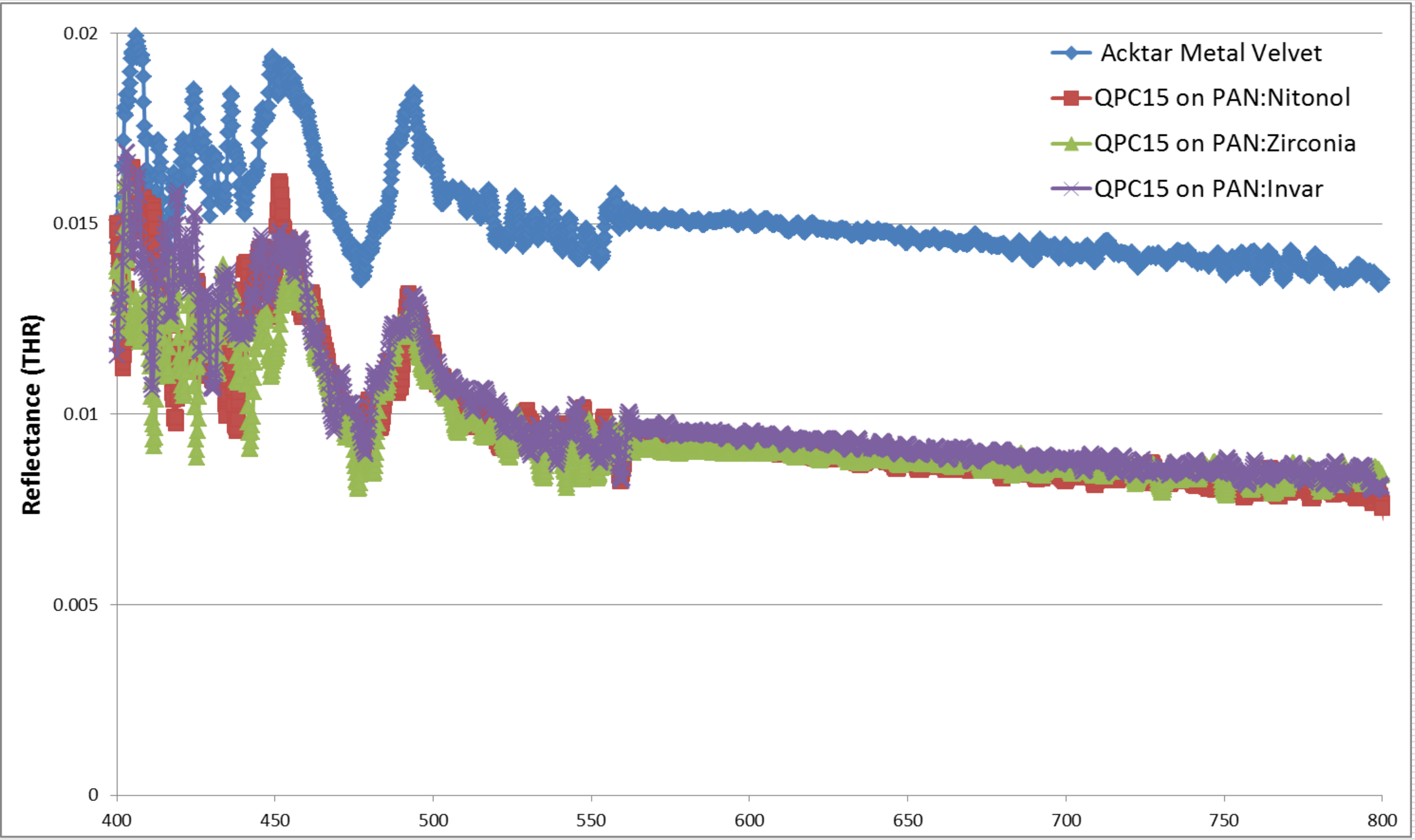


Fig. UV-Vis spectra of reflectance results composite burn-off fabricated CNT-black films as compared to Acktar performance.

Deposition on various substrates



Again, material agnostic in terms of optical performance

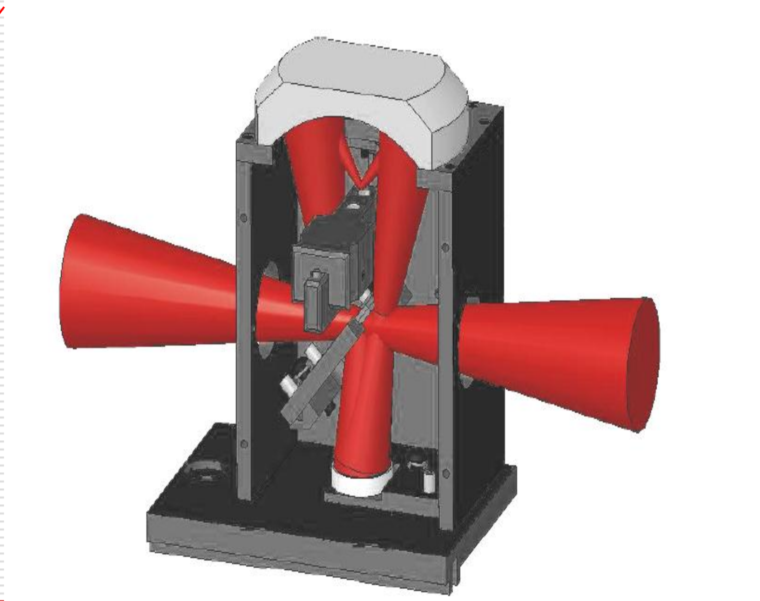
Conclusion

- We now have two methods to create highly black nanotube based coatings:
  - Wet catalysis and array growth (CVD)
  - Direct CNT deposition (paint-applied)
    - Both are
      - applicable to multiple substrates
      - good for complex parts.
      - Adherent
  - Ball Aerospace is now conducting
    - Vibration
    - Outgassing
    - Cleaning
- Questions?

DRIFTS

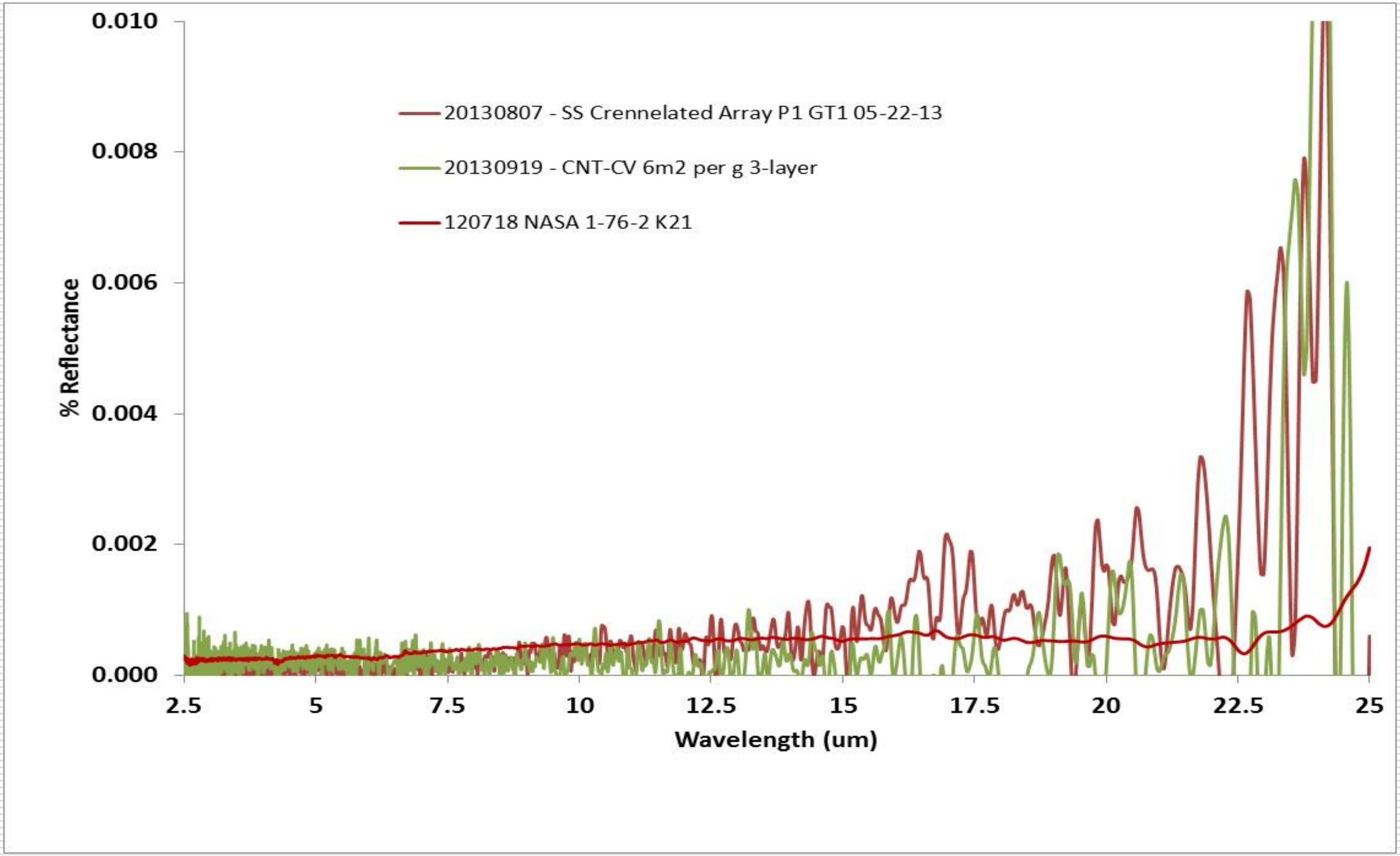
We needed a rapid method to grade the coatings in the IR. Our FTIR system, equipped with a diffuse reflectance accessory (Pike EasiDiff) gives us a way to compare the relative reflectance of our nanotube arrays.

- 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



DRIFTS

- Three avenues for array growth give 99.99+ Absorbtion



Phase Top Performers- DRIFTS