Vertically Aligned Carbon Nanotube Black Coatings for EO Applications

E. Theocharous (Theo),

Optical Metrology Group,

NPL, TW11 0LW, UK,

e.theo@npl.co.uk

C. Chunnilall, R Mole, D. Gibbs, N. Fox,

NPL, Teddington, TW11 0LW, UK,

N. G. Shang, G. Howlett, B. Jensen,

Surrey NanoSystems Ltd, Newhaven, BN9 0DQ, UK,

R. Taylor, J. R. Reveles, O. B. Harris and N. Ahmed

EnerSys ABSL, Abingdon, OX14 3ED, UK

J. Lehman

NIST Boulder, USA

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CONTENTS

The responsivity of infrared radiometers drifts!

- The responsivity of infrared radiometers used in EO applications is known to drift due to drifts in the response, the "T^2 effect", the "ice effect", etc.

- Blackbodies (BBs) are used routinely on EO missions because they provide the best means to calibrate instruments measuring **thermal infrared radiance** with lowest uncertainties.

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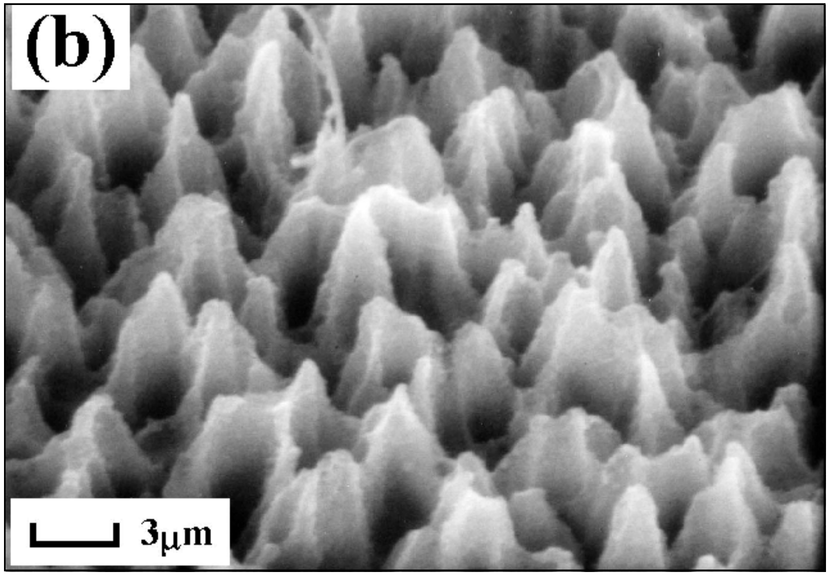
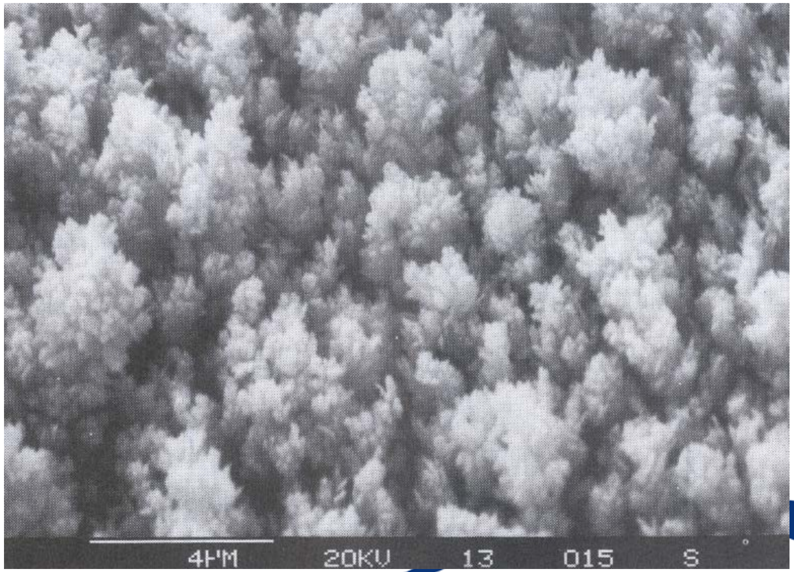
Decrease weight of on-board BBs

- EO missions require **large area BBs** in order to overfill the FoV of the radiometers.
- Large (aspect ratio) BBs are required to ensure that the BB **emissivity is** adequately **high**.
- Mass is “proportional” to size of BB.
- A highly absorbing coating will allow smaller (and therefore lighter) BB cavities to be constructed and still retain high emissivity values.

Black coatings

- Fresnel reflection provides the fundamental limitation to the absorbance of a material (for μ=1.5 the reflectance is 4%). This “loss” will always be there, irrespective of the absorbance of the body of the coating.
- By making the surface “rough”, light experiences more than one reflection before escaping, this increasing the overall absorbance of the coating.





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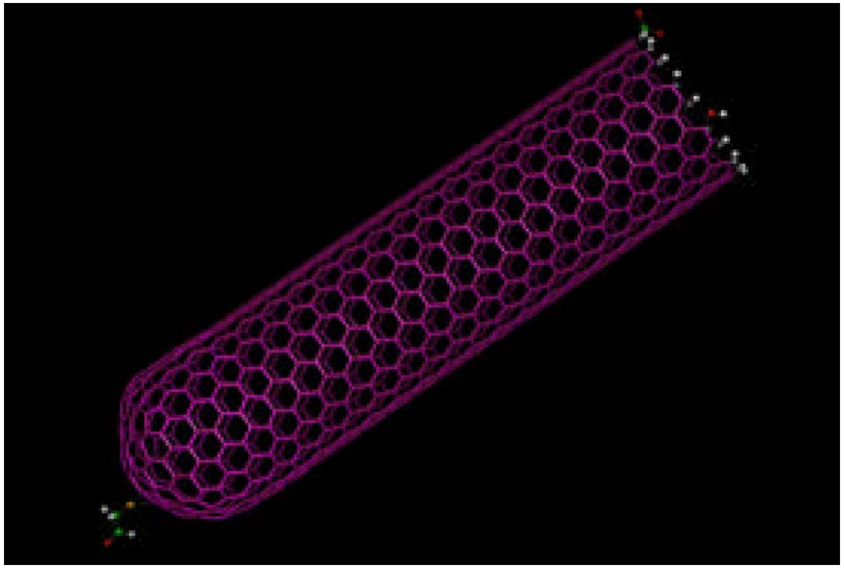
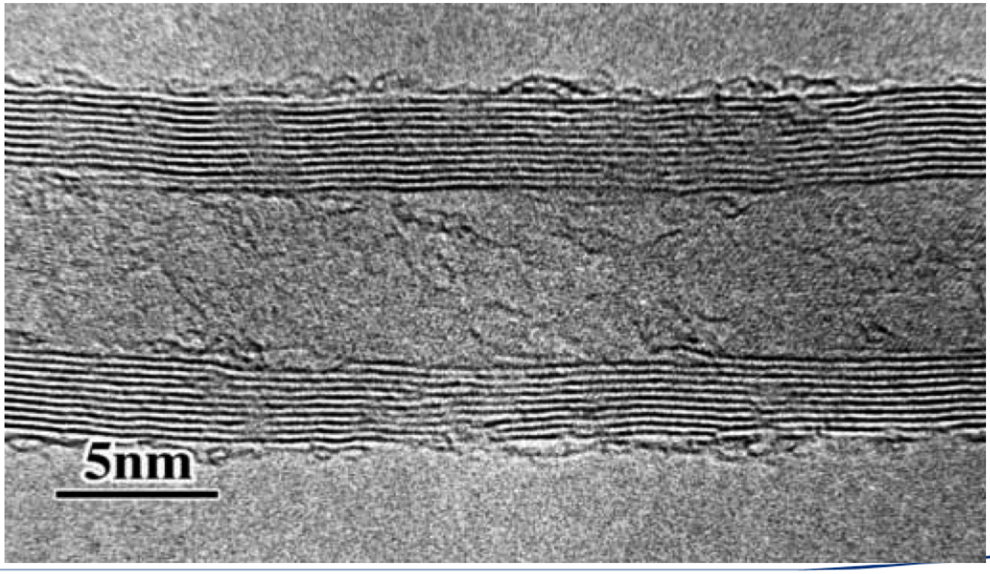
A carbon nanotube is formed by "rolling" a "sheet" of graphite into a cylinder. The figure shows a carbon nanotube structure capped at one end





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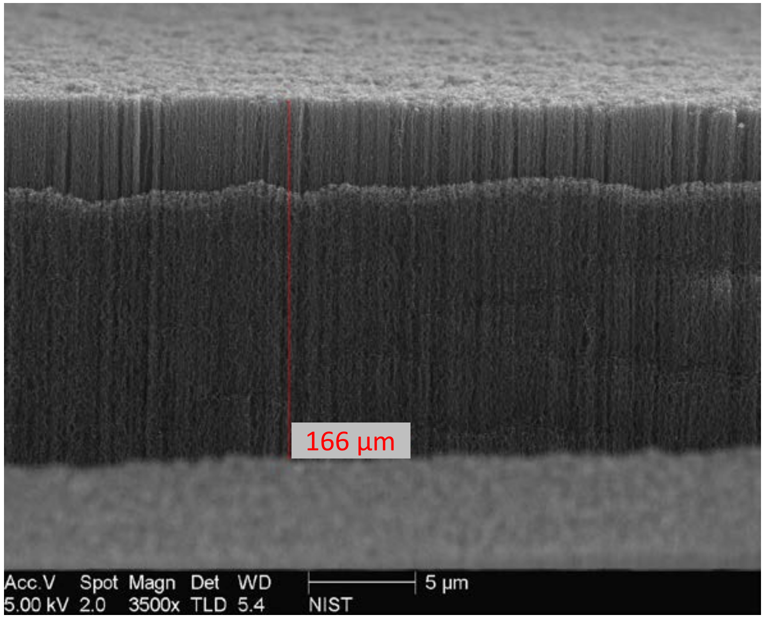
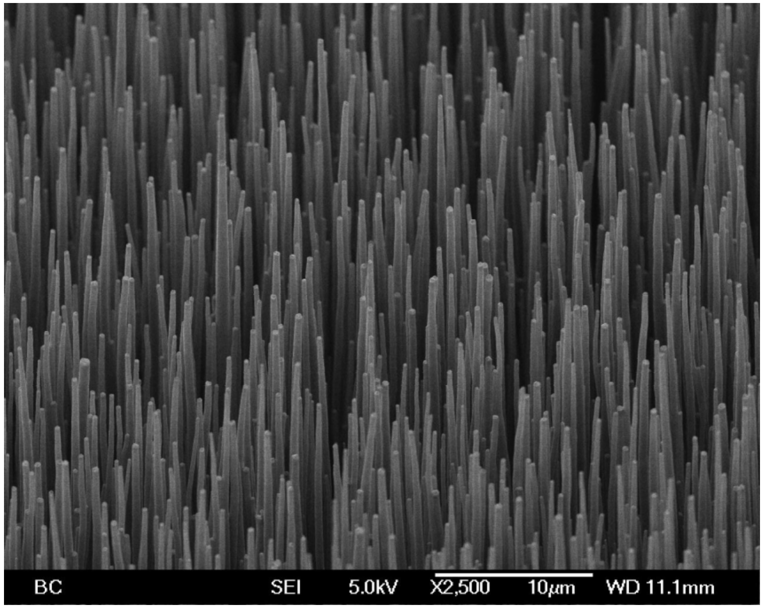
Vertically Aligned carbon NanoTube Arrays (VANTA)s





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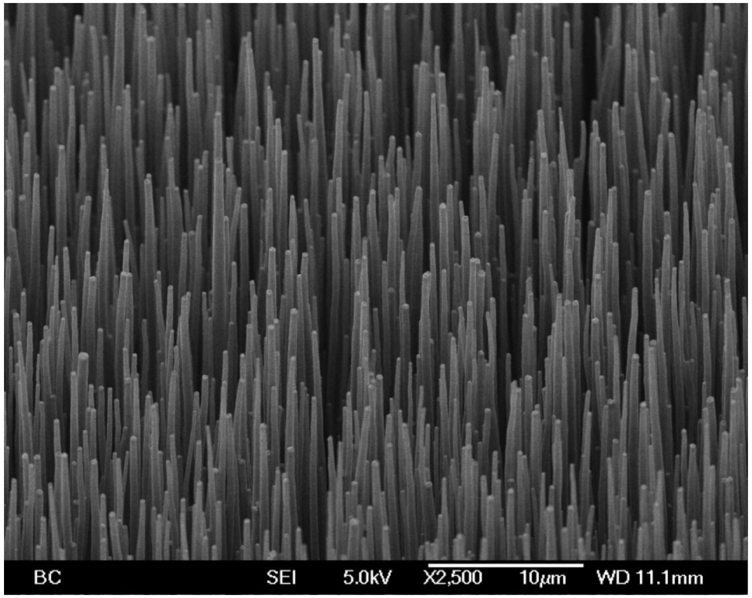
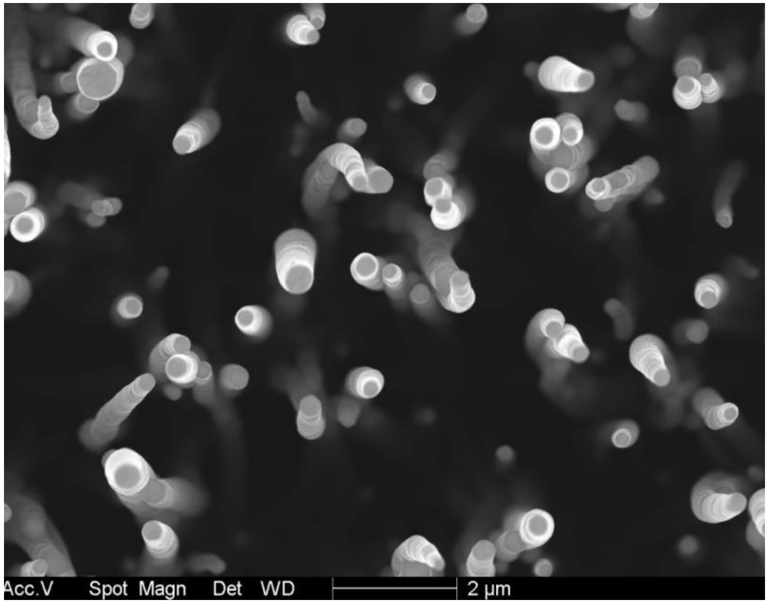
HISTORY of VANTA coatings

- In 1997 Pentry and co-workers* theoretically predicted that VANTA coatings will have very low refractive index.
- A series of publications from NPL, NIST and elsewhere showed that the reflectance of VANTA coatings is very low, confirming theoretical predictions.





*F. J. Garcia-Vidal et al., “Effective Medium Theory of the Optical Properties of Aligned Carbon Nanotubes,” Phys. Rev. Lett. **78**, 4289-4292 (1997).

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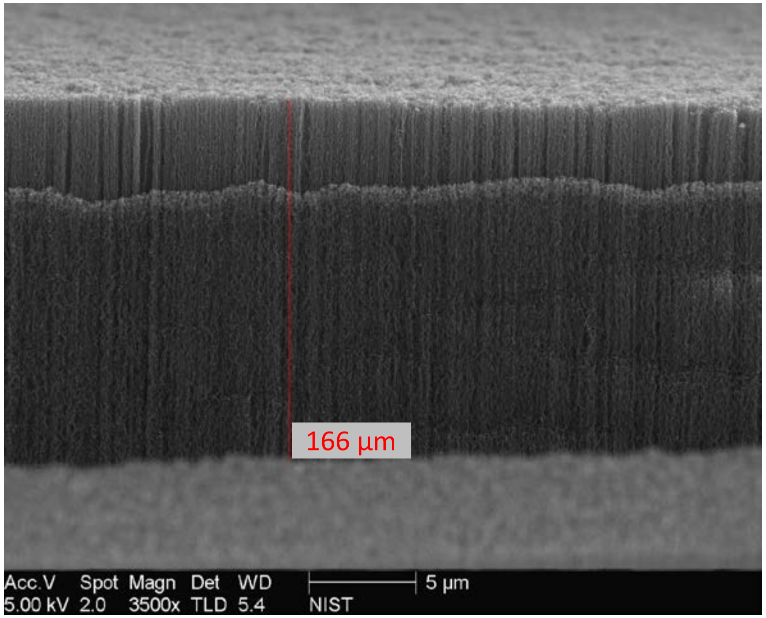
Blackest coating ever!

- Vertically Aligned carbon NanoTube Array (VANTA) coatings have been shown to have the lowest directional-hemispherical reflectance values of any coating known to man (less than 0.05% in the visible and less than 0.5% over the thermal infrared).



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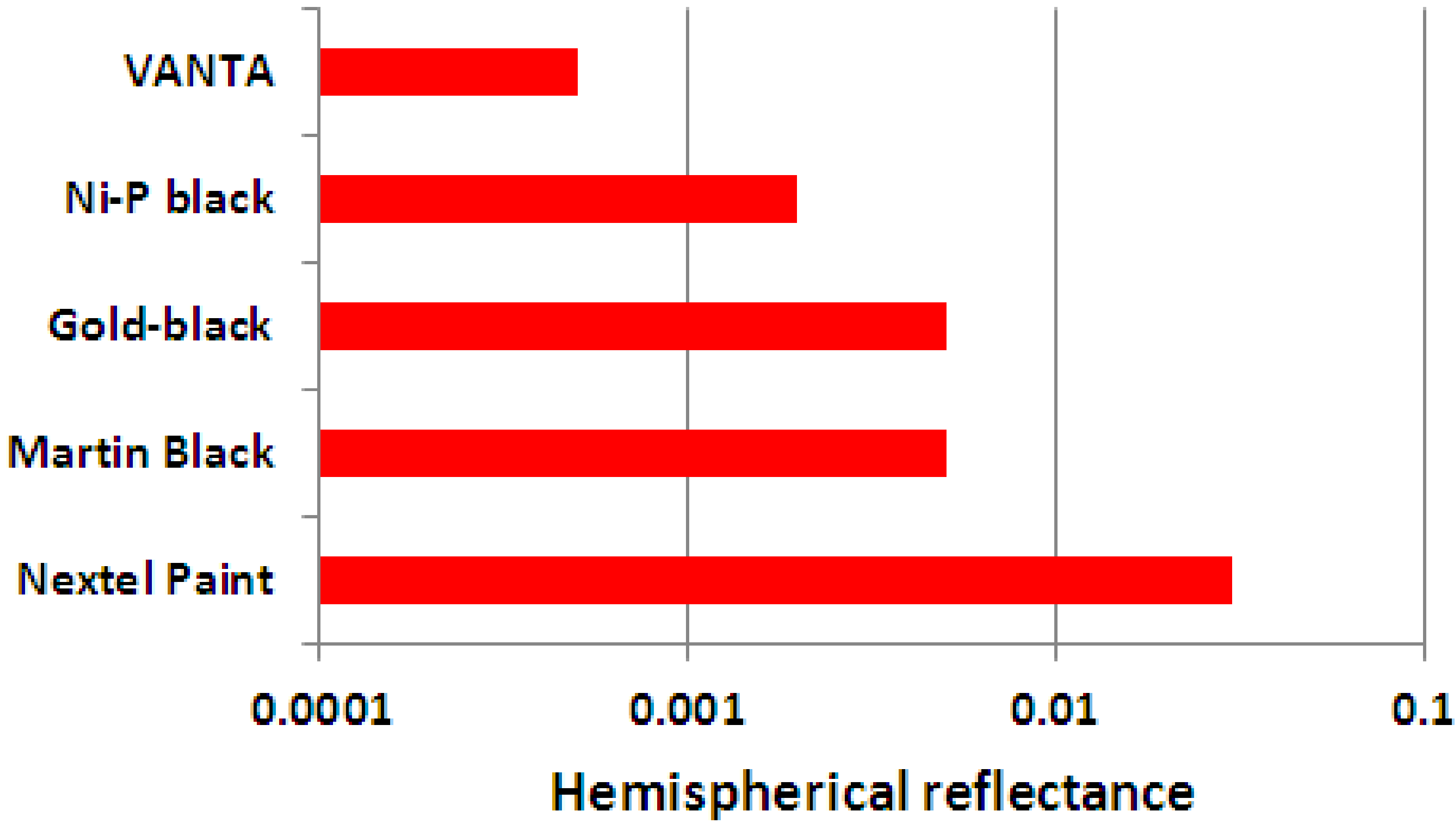
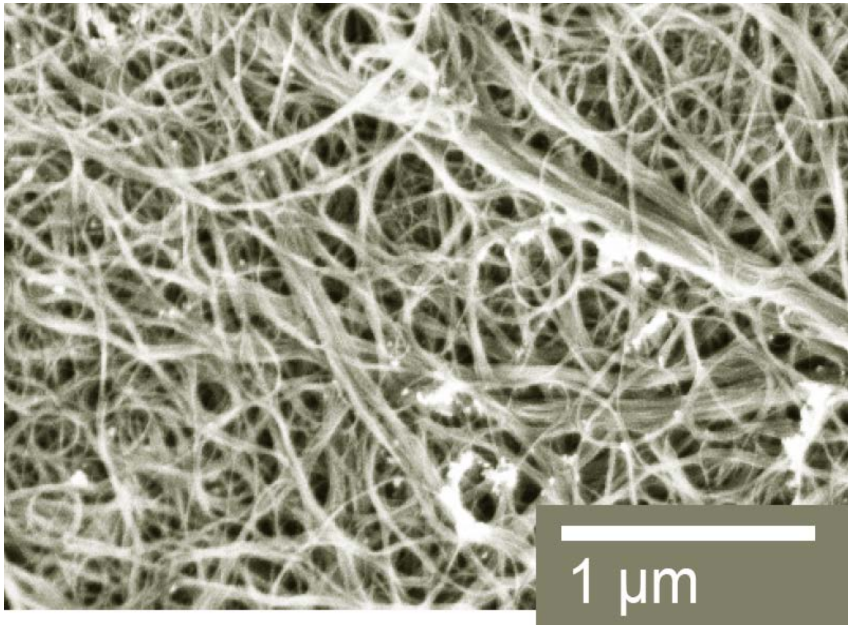
Comparison of the hemispherical reflectance of a VANTA coating with four commonly used black coatings in the visible.

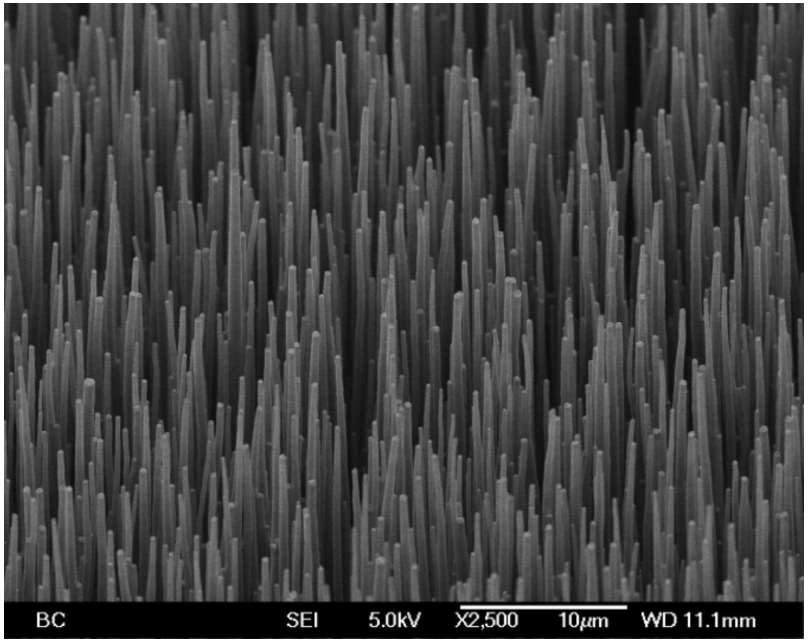


Two types of MWCNT coatings

Sprayed



Vertically Aligned



Growth of VANTAs

- VANTA coatings are grown at temperatures of 750 °C.
- So far VANTAs have been grown almost entirely on silicon substrates.
- Aluminium is the preferred material for EO BlackBody cavity applications.
- However aluminium melts at 660 °C.
- The purpose of this presentation is to tell you about:

  the growth of VANTA coatings on space-grade aluminium substrates and

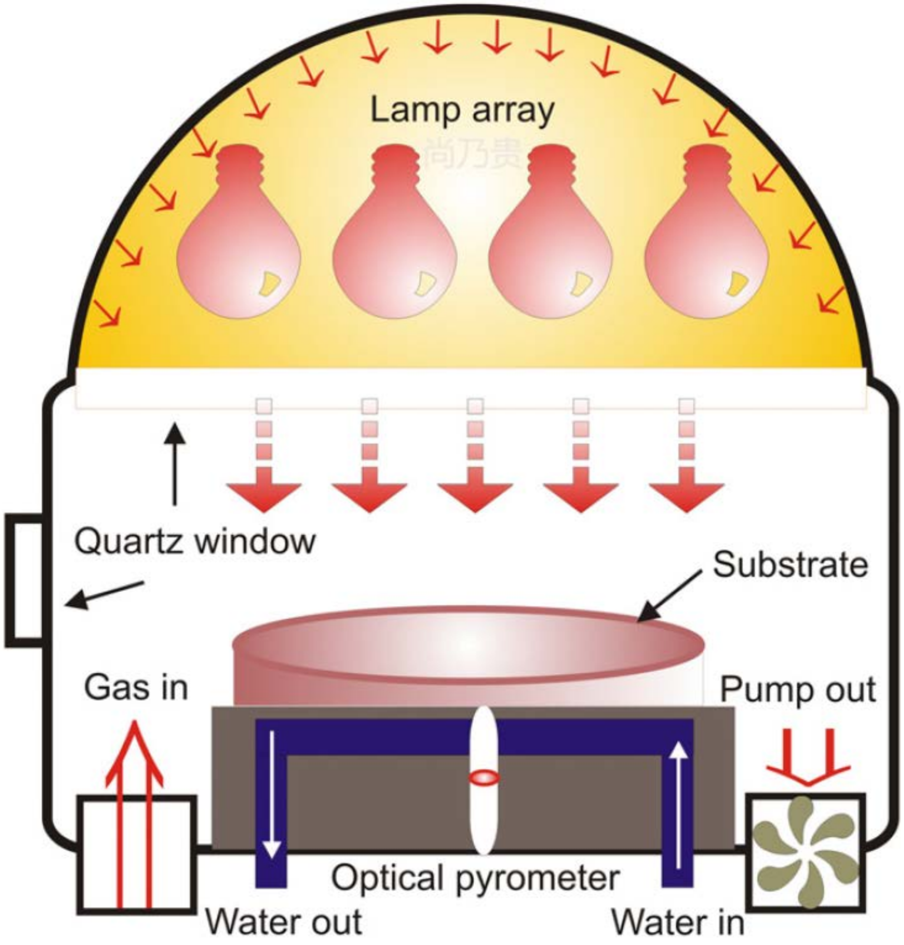
  the partial space qualification of the resulting coated samples.

How "NanoTube Black" came about

- Three UK-based companies embarked on a project to grow VANTA coatings on space-grade aluminium substrates and to space qualify the resulting products.
- Surrey NanoSystems Ltd (SNS) undertook to fabricate the samples.
- NPL measured the optical properties of the samples.
- The samples were then subjected to a number of space qualification tests by ABSL.
- NPL re-measured their optical properties to determined any deterioration in their characteristics.
- The project was partly funded by TSB.

Schematic diagram of the SNS PTCVD system

N. G. Shang et al., "High-rate low-temperature growth of vertically aligned carbon nanotubes," Nanotechnology 21, 1-6 (2010).



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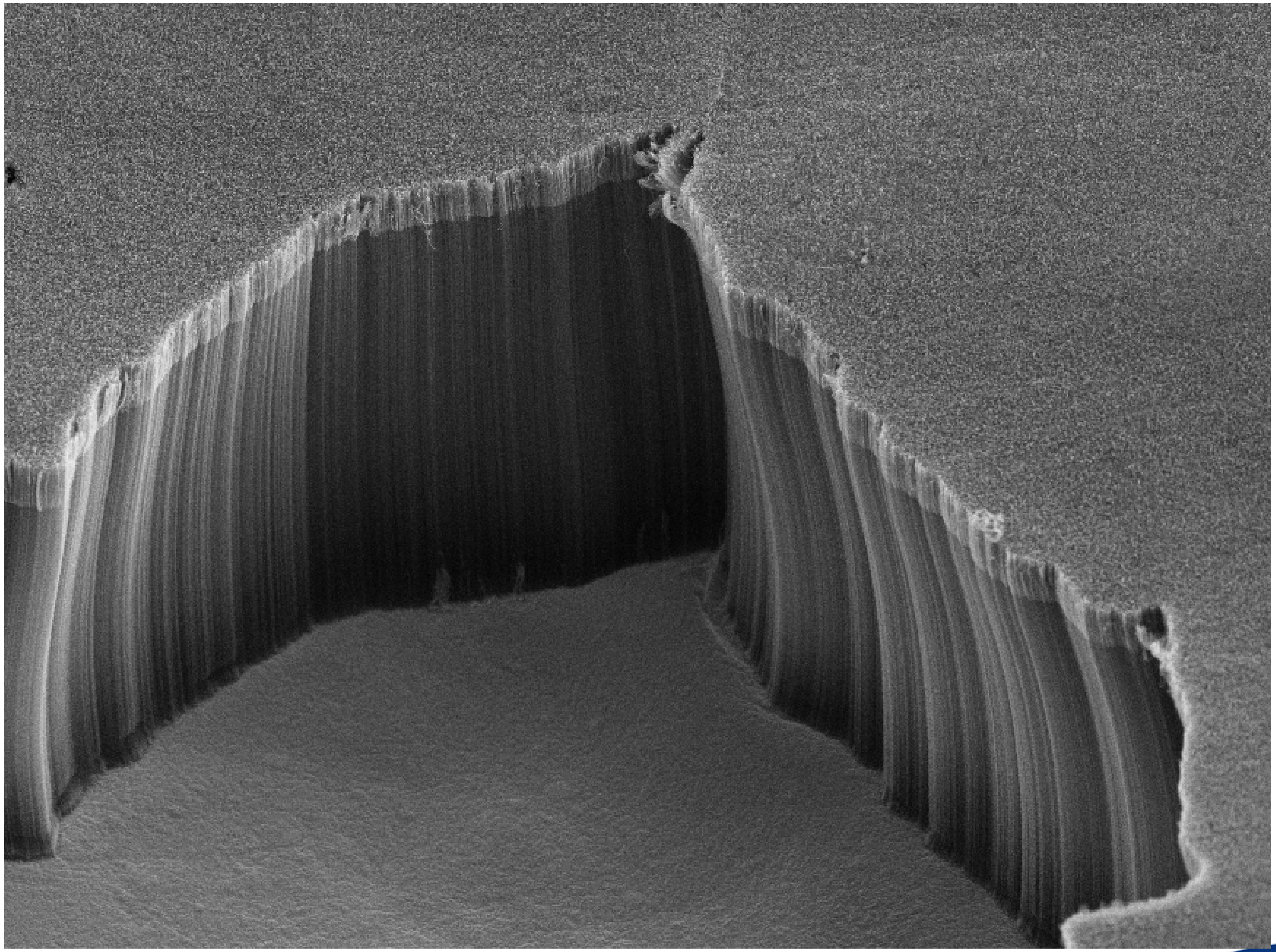
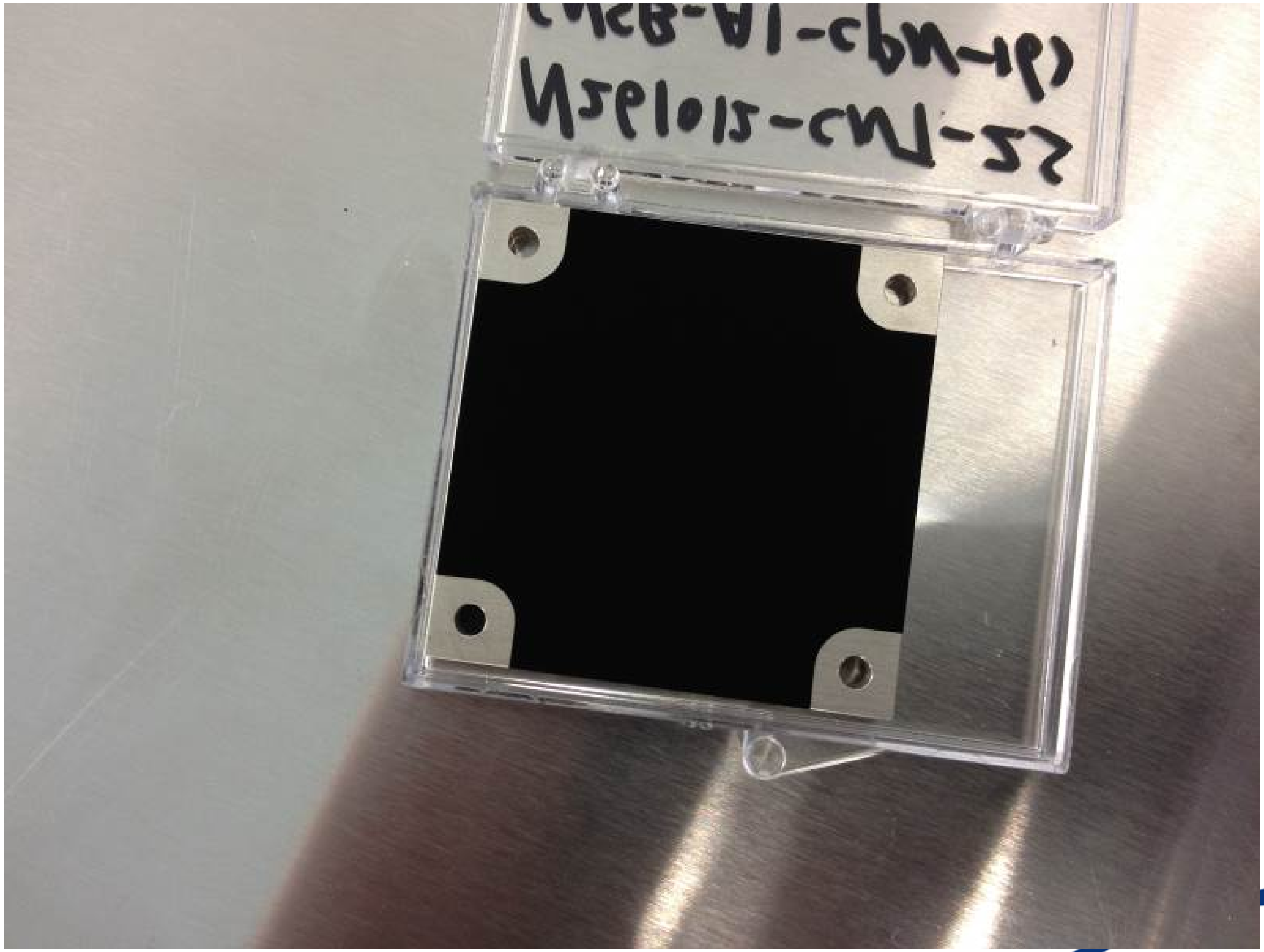
Vertically aligned CNTs grown on an Aluminium substrate.



A 50 mm by 50 mm sample of VANTA NanoTube Black grown on a space-grade aluminium substrate. The directional hemispherical reflectance of this coating is less than 0.05% in the visible.



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Fabrication of the VANTA-on-aluminium samples

- A total of six NanoTube Black samples were prepared by Surrey NanoSystems (SNS)
- Size of coupons: 40 mm x 40 mm x 3 mm.
- Type of substrate: 6061-T6 aluminium alloy.
- Thickness of VANTA coatings ranged from 22 µm to 44 µm.
- The coupons were chemically cleaned prior to the deposition of a multi-layer barrier/catalyst, designed to ensure robust adhesion of the CNTs to the substrate.
- The samples were then subjected to an activation step under a reducing atmosphere at 450 °C.
- Growth was in a CVD reactor configured for plasma-assisted, **photo-thermal** chemical vapour deposition (PTCVD).
- The PTCVD process provides rapid top-down heating of the catalysed surface of the sample, whilst cooling of its support platen.

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FABRICATION (continued)

- The use of the SNS growth method allows the higher catalyst temperatures required for low defect, aligned growth at controllable CNT mass density to be reached, whilst preventing melting of the aluminium substrate.

- Different lengths of MWCNT (VANTA) coatings can be grown on the coupons by varying the growth time.

Characterisation and testing

- The structure and morphology of the deposited CNT films on the aluminium coupons was characterised by Raman scattering and scanning electron microscopy.
- The directional-hemispherical reflectance of the six samples was measured using the NPL infrared hemispherical reflectance facility [C. Chunnilall and E. Theocharous, "Infrared hemispherical reflectance measurements in the 2.5 μm to 50 μm wavelength region using an FT spectrometer," Metrologia **49**, S73-S80 (2012)].
- Five of the VANTA-coated samples were then sent to ABSL where they were subjected to the space qualification tests whilist the sixth sample was retained by NPL as a control.
- On completion of the space qualification tests, the NanoTube Black samples were returned to NPL for re-measurement of their hemispherical reflectance. The control was also re-measured at this time.

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Space Qualification Tests completed:

- **The space qualification tests included:**
  - mass loss tests,
  - outgassing tests,
  - vibration tests,
  - shock tests and
  - thermal cycling tests.

Space Qualification Tests

- The mass loss and outgassing test consisted of the samples being analysed under vacuum by a residual gas analyser. No molecular species were detected at significant levels other than water, which would be driven off by the preliminary bake-out.
- The vibration test was completed in a class 100 environment.
- The thermal cycling test involved the thermal cycling of the test samples between -100 ^{o}C and +100 ^{o}C for 6 full cycles
- It also included repeated immersion in liquid nitrogen.

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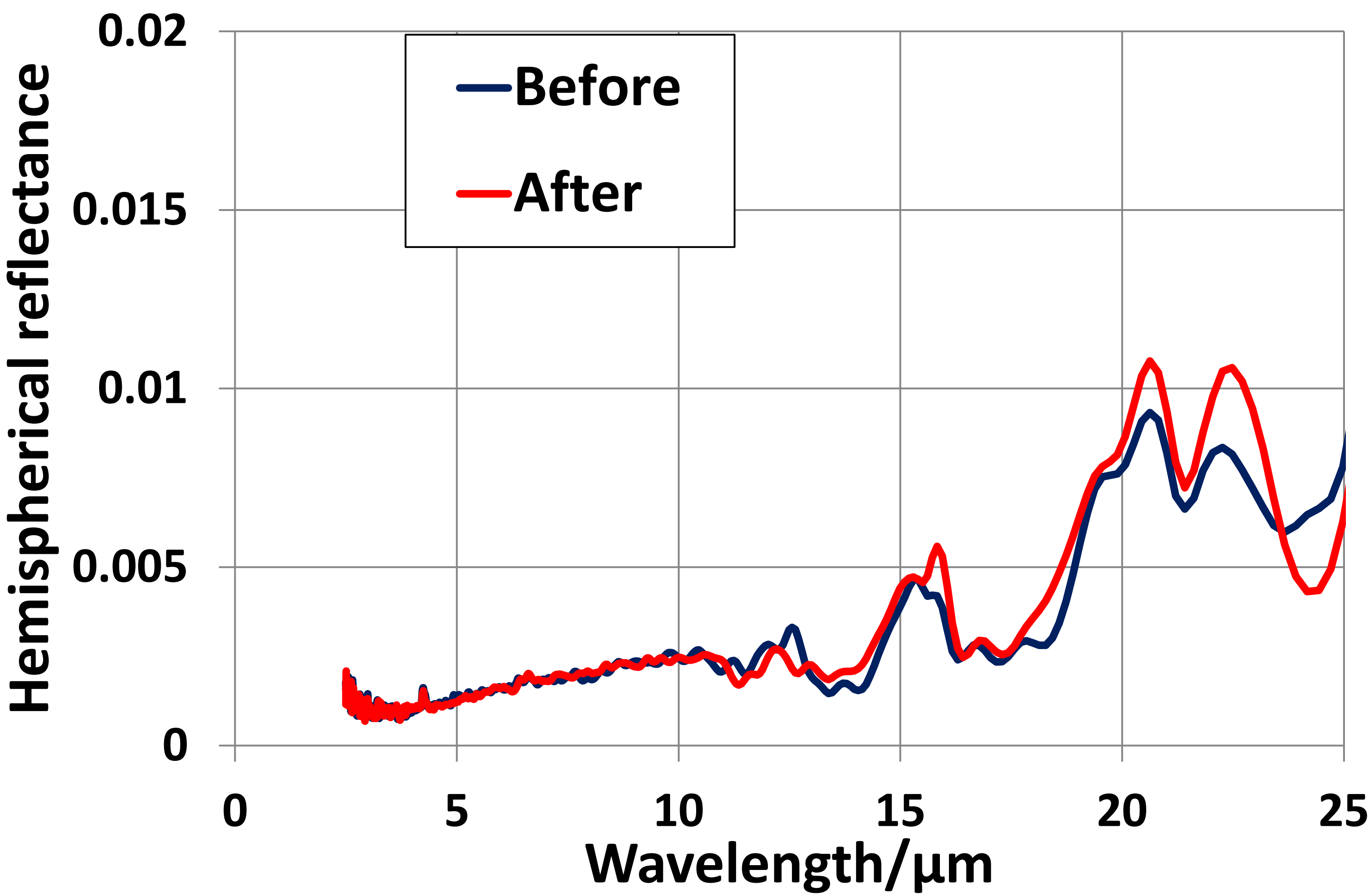
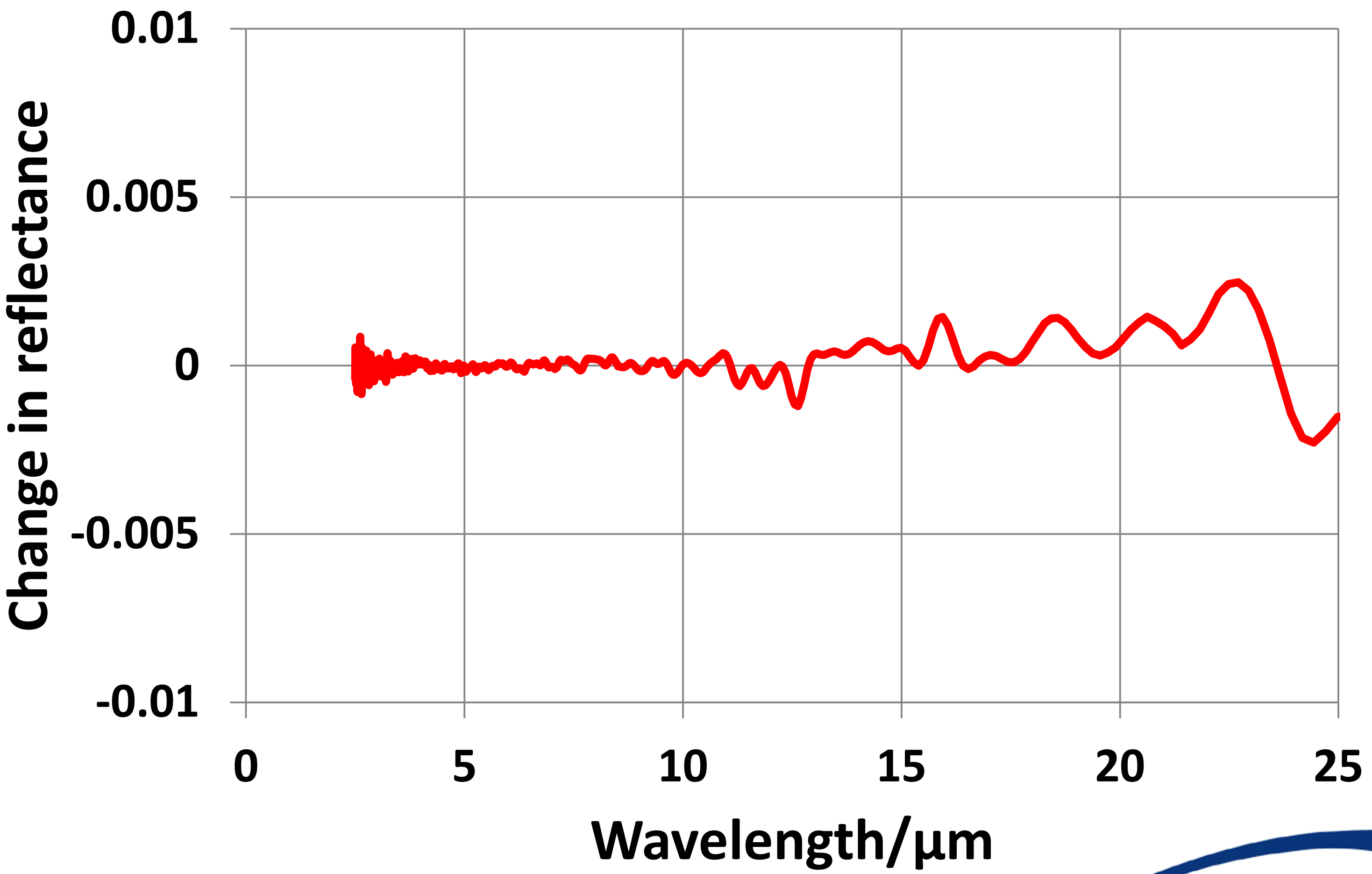
Hemispherical reflectance of sample 5 measured before and after the space qualification tests.



Absolute change in the hemispherical reflectance of sample 5 due to the space qualification tests



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Discussion

- The uncertainty in the measurement of hemispherical reflectance of the test samples was 0.0045 (*k*=2) [see "Infrared hemispherical reflectance measurements in the 2.5 μm to 50 μm wavelength region using an FT spectrometer" Metrologia, **49**, S73-S80, 2012].
- The difference in the reflectances of the samples before and after the space qualification tests was within the sum of the uncertainties of the two measurements (before and after the space qualification tests).
- We can conclude that no changes in the hemispherical reflectance of these samples were observed as a result of the space qualification tests.
- Measurements on the control samples (the samples not subjected to the space qualification tests) confirm that there was no significant change in the reflectance data during the period of the space qualification tests.

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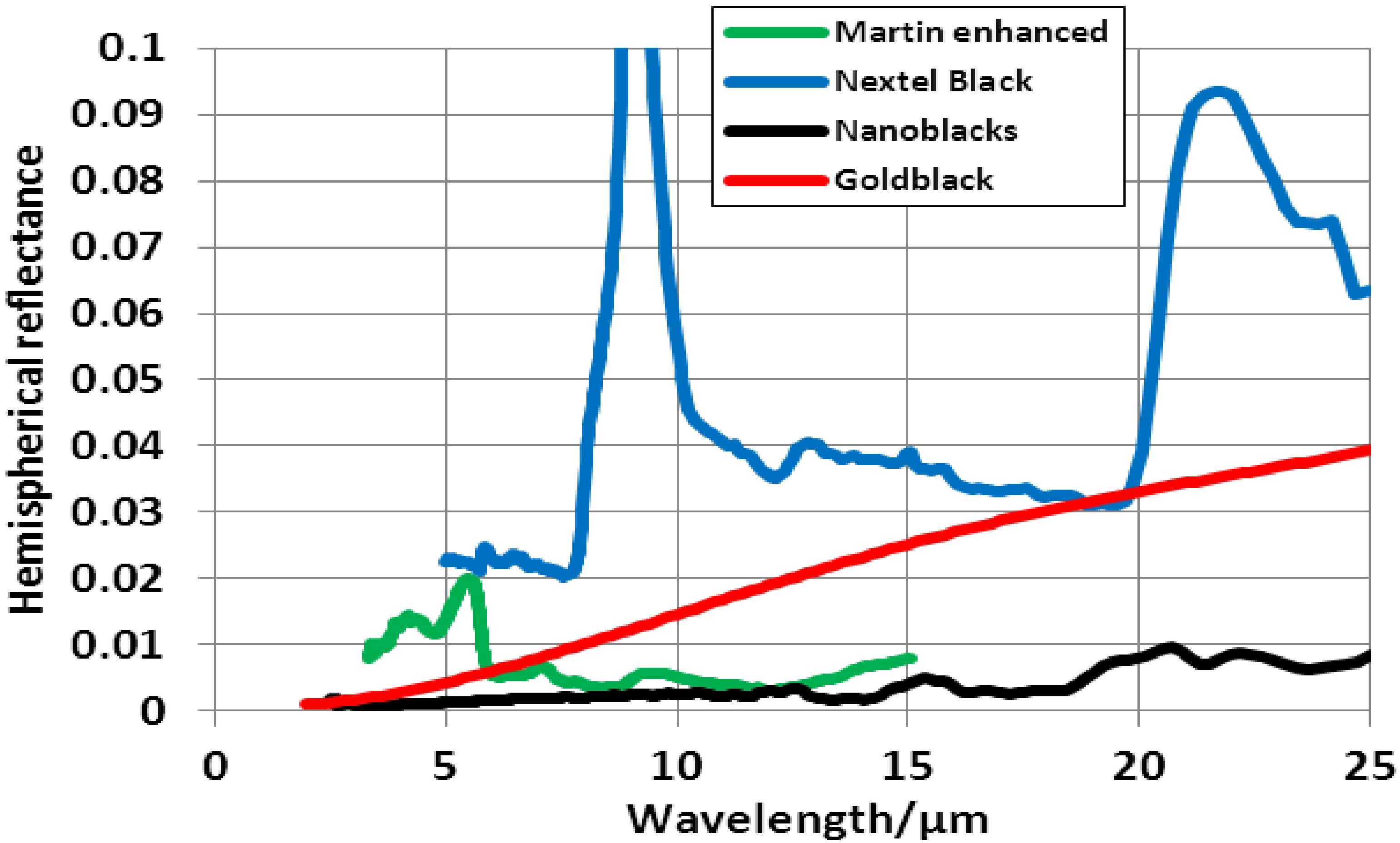
For further information on VANTA coatings on aluminium substrates see:

E. Theocharous et al.,

"The partial space qualification of a vertically aligned carbon nanotube coating on aluminium substrates for EO applications"

Optics Express, 22, 7290-7307, 2014

Comparison of the hemispherical reflectance of a VANTA coating with three commonly used black coatings.



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Other EO applications

- VANTA coatings can also be used in other EO areas where black coatings (usually black paints) are currently used.
- These include:
  - Coatings for baffles in EO instruments.
  - Coatings for the suppression of stray light
  - Coatings for thermal detectors

Coatings for baffles in EO applications

ESA have called for bids for a contract to evaluate novel black coatings for baffles for the 400 nm to 2.5 µm wavelength range. This is aimed at the evaluation of VANTA coatings!

NASA is already using VANTA coatings (**grown on a silicon substrate**) to coat both sides of the 600 µm wide slit of the "Ocean Radiometer for Carbon Assessment" (ORCA) in order to reduce stray light [Quijada et al., "Optical component performance for the Ocean Radiometer for Carbon Assessment (ORCA)," Proc. SPIE 8153, Earth Observing Systems XVI, 10.1117/12.895938 2011].

However, the slit itself was **fabricated from silicon**, which is brittle and poorly suited to space applications. Silicon was chosen to provide a suitable surface for Carbon NanoTube (CNT) adhesion, and its ability to withstand the high temperatures (750 °C) required in conventional for CNT growth.

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Coatings for thermal detectors for EO

- Missions like GERB and the Broad Band Radiometers (due to fly on the EarthCARE mission) require detectors with a flat spectral responsivity (and low thermal mass).
- VANTA coatings fulfil these requirements better than any other black coating known to man!
- Lithography can be used to define the shape of the area covered by VANTA.
- VANTA coatings have high thermal conductivity, and low thermal capacity so they are well suited for thermal detector applications.
- VANTA coatings have been grown directly on $LiTaO_3$ pyroelectric crystals (to satisfy my requirements for relative spectral responsivity standards in the infrared).

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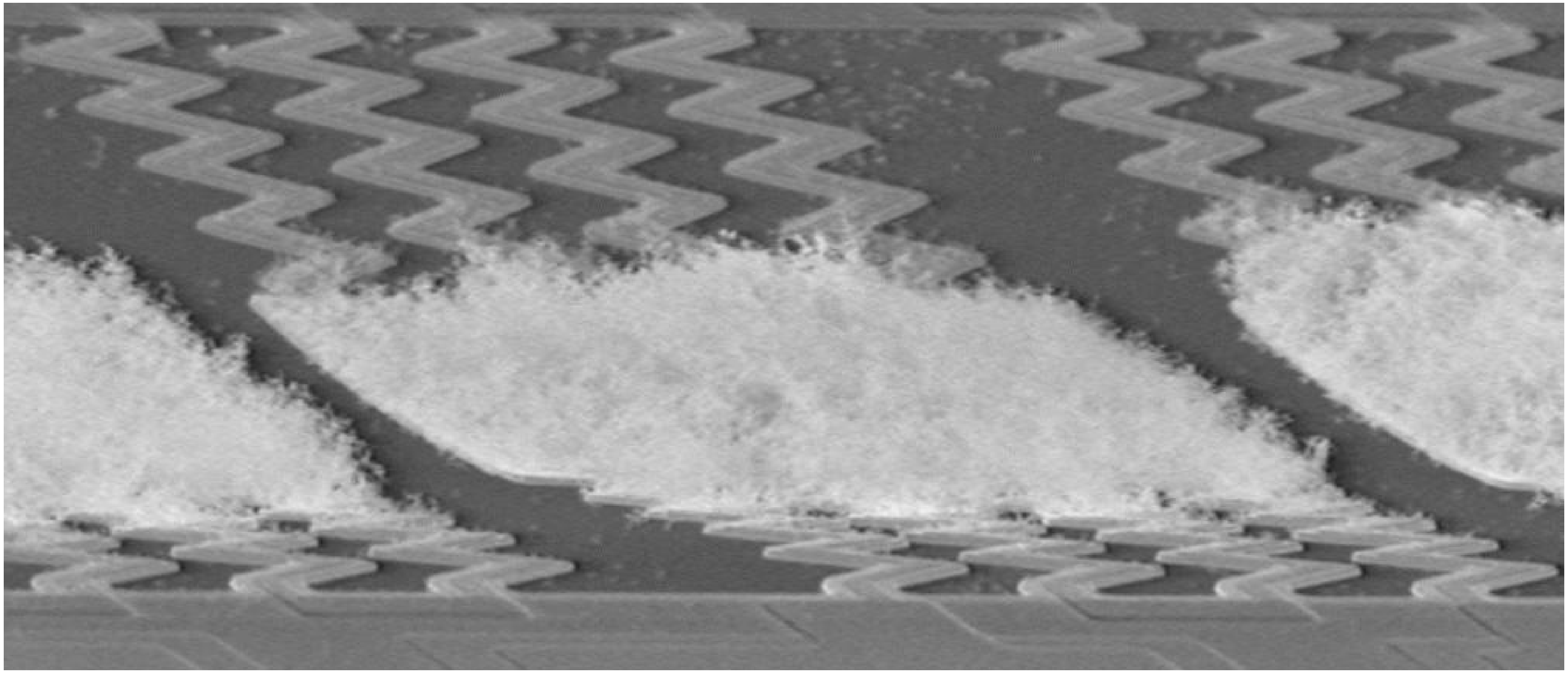
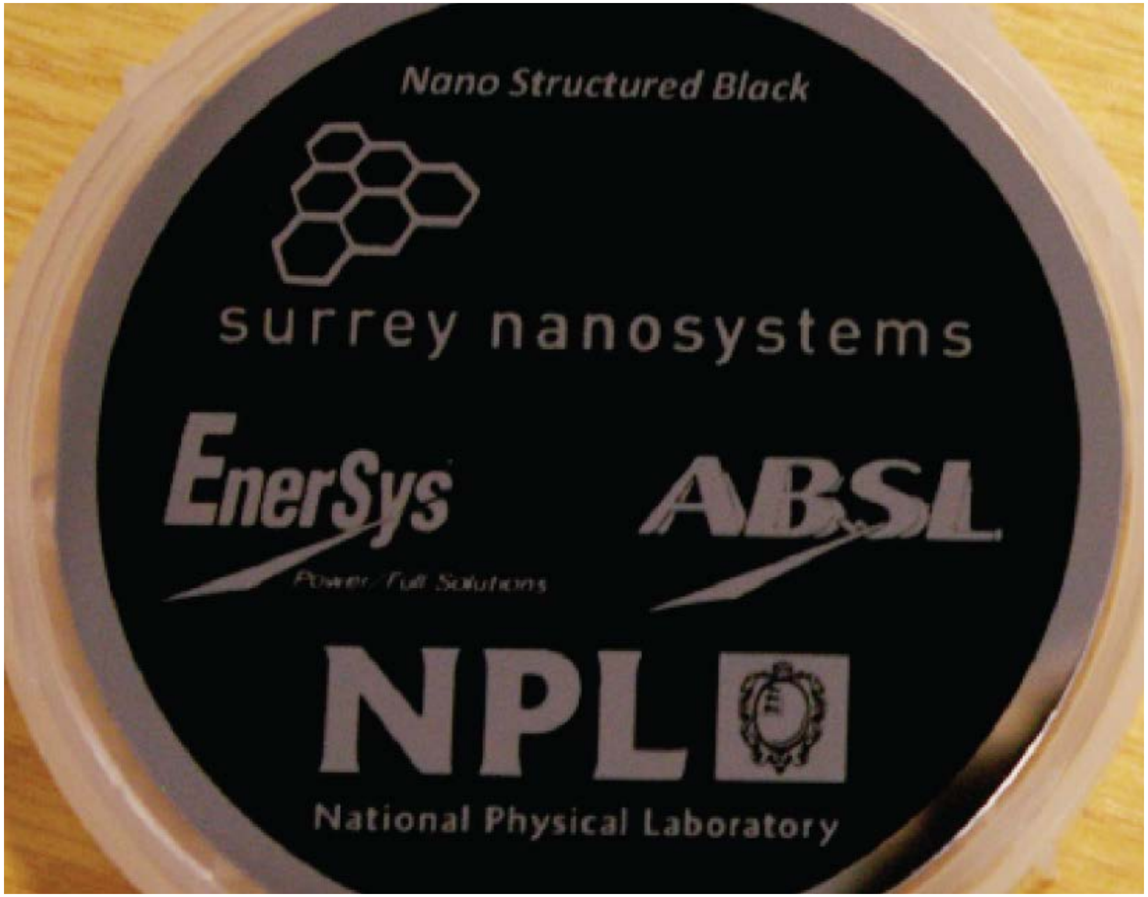
SEM of pixels of the GERB detector array coated with a gold-black coating (provided by G. Butcher, Leicester University).



Nanotube Black VANTA coating showing the logos of the partners who develop this VANTA coating.



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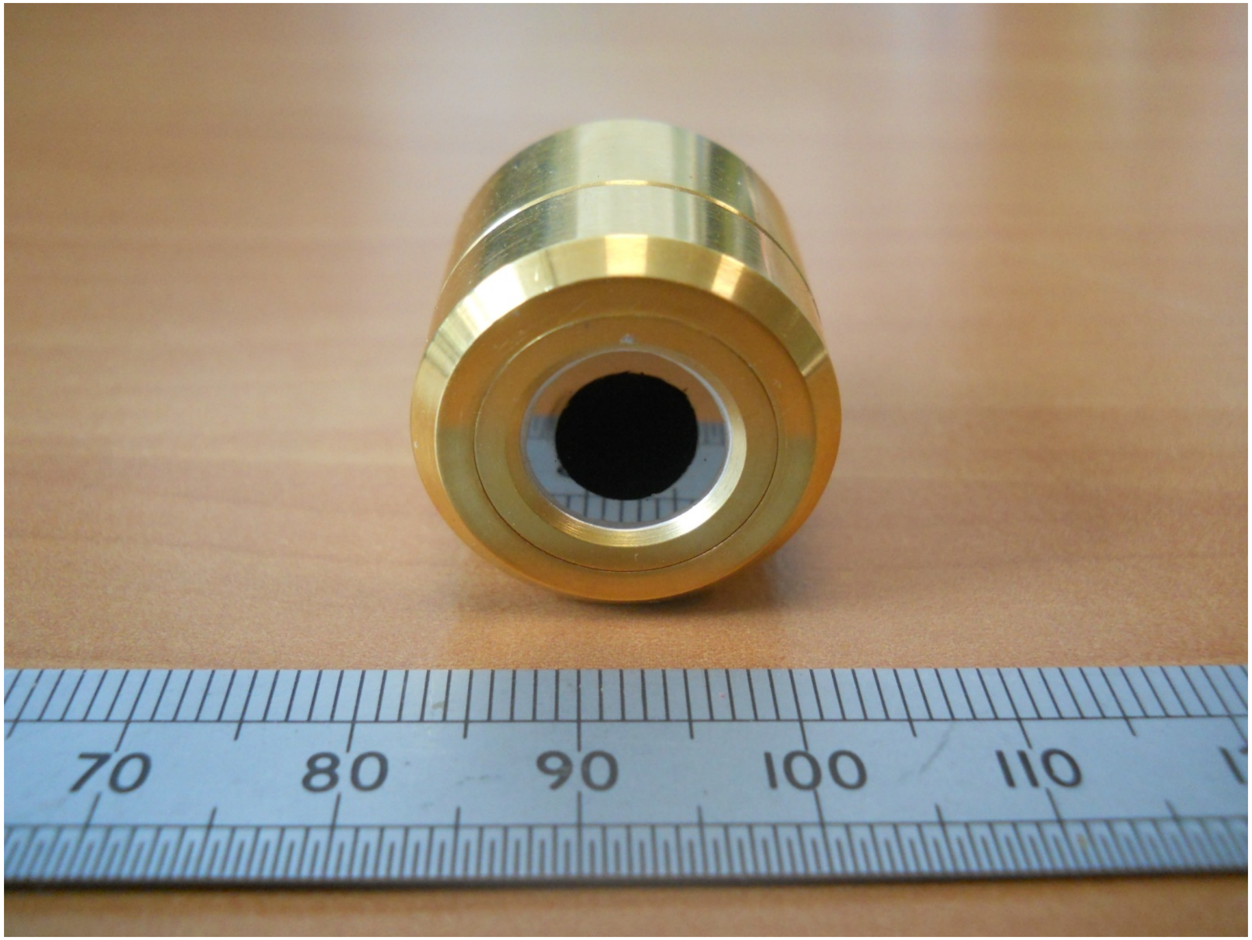
NanoTube Black VANTA-coated $LiTaO_3$ pyroelectric detector.



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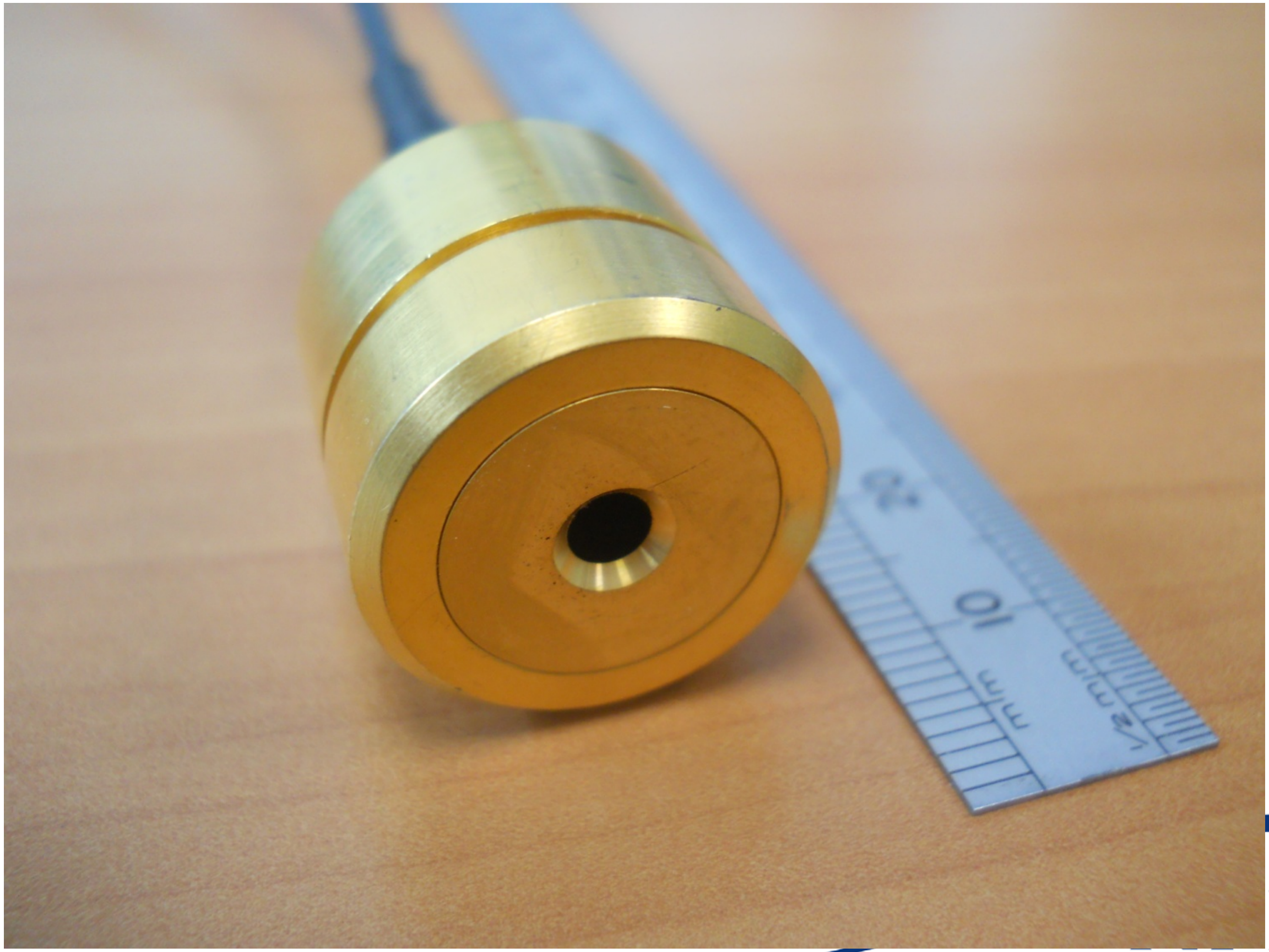
NanoTube Black VANTA (on Si)-coated LiTaO3 pyroelectric detector.

E. Theocharous, S. P. Theocharous and J. H. Lehman, “Assembly and evaluation of a pyroelectric detector bonded to vertically aligned multiwalled carbon nanotubes over thin silicon”, Applied Optics, 52, 8054-8059, 2013



Condition	Suitability of NanoTube Black
The coating must have high thermal conductivity to ensure that the temperature at the "air" (vacuum) side of the coating does not differ significantly from the temperature of the substrate.	This is required in order to ensure that the temperature drop across the black coating is small. NanoTube Black has excellent thermal conductivity across the thickness of the coating - carbon nanotubes have been shown to have very high thermal conductivity along their length, typically 6600 W m^{-1} K^{-1} .
Good thermal stability and repeatable optical performance after thermal cycling	The samples were subjected to a number of temperature cycles between -100 °C and 100 °C without any observed degradation. Further tests involving immersion in liquid nitrogen (-196 ^{o}C) also showed no degradation.
Resistant to the launch vibration and staging shock.	Vibration and shock tests carried out in the current study demonstrate that the coating satisfies this requirement.
Resistance to chemical attack such as the atomic oxygen encountered in low earth orbit, as well as resistance to moisture.	This was not investigated in the current study.
The coating must have low outgassing.	Outgassing tests carried out in the current study confirm that NanoTube Black coatings satisfy this requirement.
The coating must have low "particle generation" i.e. fragments of the black coating must not be dislodged, thus altering the characteristics of the black coating and depositing on nearby optical surfaces, causing their degradation.	There was no significant loss of mass of the coatings after the samples were subjected to the vibration and shock tests, confirming that NanoTube Black coatings satisfy this requirement.

Easy to fabricate on complex geometries	Areas up to 200 mm by 200 mm can currently be coated. The growth of VANTA coatings on curved surfaces/3D objects was not investigated in the current study. Growth on Al foil has been done.
Manufacturing repeatability.	Unlike chemical etching, the procedure used to grow NanoTube Black is very controlled and the results are repeatable.
Long-term storage/stability/durability.	No long term degradation test have so far been carried out but the nature of NanoTube Black coatings implies good long term stability, unlike some other black coatings such as gold-black whose structure is known to collapse under certain storage conditions.
Coating availability; International Traffic in Arms Regulations (ITAR) restrictions and manufacturability.	Difficulties in acquiring ITAR-controlled black materials are overcome with the development of the NanoTube Black coating.
Cost (less critical for space applications).	The superior absorbance of NanoTube black allows much smaller blackbody cavities than other black finishes, meaning that a higher per-unit-area cost for NanoTube black is offset by a smaller area to be coated.
Ideally the coating must be able to coat any substrate.	So far VANTA coatings have been grown on a variety of substrates and there is no reason to prevent its deposition on stable substrates whose melting point is above 450 °C.

Conclusions

- VANTA coatings have been grown on space-grade aluminium substrates using a novel growth method.
- The directional-hemispherical reflectance of the resulting coatings is low (less than 0.05% in the visible and less than 0.5% below 20 µm).
- The reflectance charcateristics of the samples did not change after the samples were subjected to a series of space qualifications tests.

* **These coating are available to purchase.**

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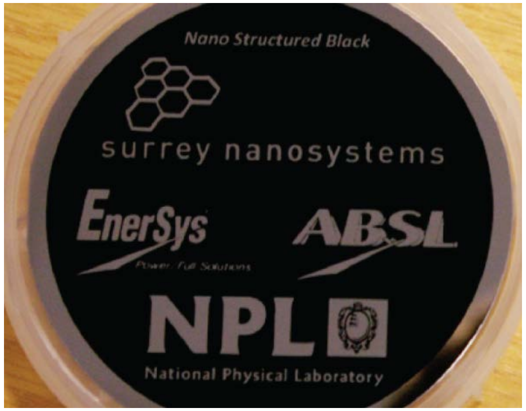

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