# Initial Studies of the Bidirectional Reflectance Distribution Function of Multi-walled Carbon Nanotube Structures for Stray Light Control Applications

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## The Application of Low Reflectance Surfaces in Optical Instruments

- Low reflectance surfaces have wide application in optical instrument design
  - Detectors
  - Beam dumps
  - Solar collection applications
  - Beam dumps
  - Baffles, vanes, and stops
  - Housings
- The choice of low reflectance surface is strongly application driven
  - Operating wavelength range of instrument
  - Angles of incidence and reflectance as defined by instrument's optical configuration
    - Specular surface
    - Diffuse surface
  - Substrate material
  - Environment in which the surface is to be deployed
- This talk will focus on the application of low reflectance surfaces for stray/scattered light control in spaceflight instrumentation

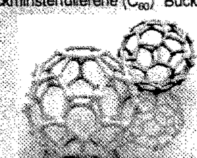
## The Study of the Optical Properties of Low Reflectance Surfaces in Spaceflight Instrumentation has a Long History

- Low reflectance surfaces have included the following:
  - Paints: Aeroglaze/Chemglaze Z30x products; Akzo "Cat-a-lac"products, et al.
  - Surface treatments: Various black anodizations (e.g. Martin Black, Infra-black et al.), depositions (e.g. Ball Black/NBS Black or NiP Black, Electro-less Ni, et al.)
- Fortunately, there are many good reviews and databases available on the reflectance of these surfaces
  - M.Bass, ed., Handbook of Optics-Third Edition, Vol. IV, "Chapter 6: Characterization and Use of Black Surfaces for Optical Systems," pp. 6.1-6.67 (2010).
  - Stellar Optics Research International Corporation (SORIC) data base of optical scatter data; S.H.C.P. McCall, et al.

## Multi-Walled Carbon NanoTubes (MWCNTs): a Type of Fullerene

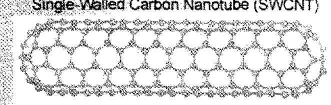
- ***Fullerene: any molecule composed entirely of C, in the form of a hollow sphere, ellipsoid or tube.***

Buckminsterfullerene ($C_{60}$) "Buckeyball"



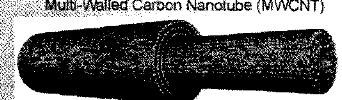
-1965: $C_{60}$ first mentioned as a possible structure by H.P. Schultz in J. Org. Chem., 30, pp. 1361-1364.
-1985: $C_{60}$ produced and detected by TOF-MS by H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley in Nature, 318, pp. 162-163, resulting in Kroto, Curl, and Smalley winning the 1996 Nobel Prize in Chemistry.

Single-Walled Carbon Nanotube (SWCNT)



-1993: SWNCT's reported by NEC (April 23) and IBM (May 24) in S. Iijima and T. Ichihasi, Nature, 363, pp. 603-605 and D.S. Bethune, C.H. Kiang, M.S. DeVries, G. Gorman, R. Savoy, J. Vazquez, et al., Nature, 363, 335-349, respectively.

Multi-Walled Carbon Nanotube (MWCNT)



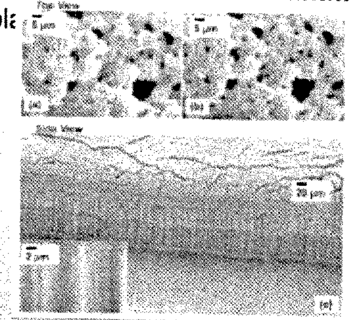
-1952: Published TEM images of 50 Å dia. C nanotubes by L.V. Radushkevich and V.M. Lukyanovich in Soviet Journal of Physical Chemistry, 24, pp. 88-95.
-1991: C nanotubes produced and detected using electron microscopy by S. Iijima in Nature, 354, pp. 56-58.
*-2006: M. Monthioux and V. Kuznetsov, "Who should be given credit for the discovery of C nanotubes?" Carbon, 44, pp. 1621-1623.*

## Research Objectives

- Develop and apply MWCNTs to spacecraft instrument components and realize an improvement of a factor of 10 in reflectance over current surface treatments
  - Stage 1: tuning nanotube geometry on Si substrate to produce a 10x decrease in total and bidirectional reflectance
  - Stage 2: improve adherence onto Si
  - Stage 3: demonstrate adherence and optical performance on nanotubes on spacecraft instrument materials (e.g. Ti)
- This is not the first study of the optical properties of MWCNTs:
  - W.A. deHeer, et al., "Aligned C Nanotube Films: Production and Optical and Electronic Properties," Science, 268, 845-847 (1995)
  - F.J. Garcia-Vidal, et al., "Effective Medium Theory of the Optical Properties of Aligned C Nanotubes," Phys. Rev. Lett., 78, 4289-4292 (1997)
  - Z.P. Yang et al., "Experimental Observation of an Extremely Dark Material Mde by a Low Density Nanotube Array," Nanoletters, 8, 446-451 (2008)
  - X.J. Wang, et al., "Visible and Near-Infrared Radiative Properties of Vertically Aligned Multi-walled C Nanotubes," Nanotechnology, 20, 215704 (9 pp.) (2009).
- We hope to perform the necessary engineering to make MWNCTs sufficiently robust to be used in spacecraft instrument stray scattered light control applications while maintaining optical performance over the uv to shortwave ir wavelength region
  - Optical performance is monitored using $8^0$ hemispherical reflectance and bidirectional reflectance distribution function (BRDF) measurements

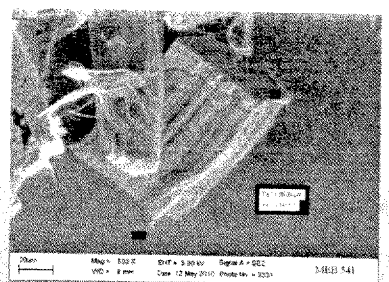
## MWCNT Samples (1 of 3)

- Fabrication of vertically oriented MWCNT films was accomplished by catalyst-assisted chemical vapor deposition (CVD)
  - Al/Fe thin film thermally deposited on Si followed by exposure to $H_2C=CH_2$ feedstock gas at $750^0C$ in a reducing environment.
  - Varying catalyst thickness modulates MWNCT height
  - Sample: MWCNTs on Silicon substrate treated with oxidizing pl



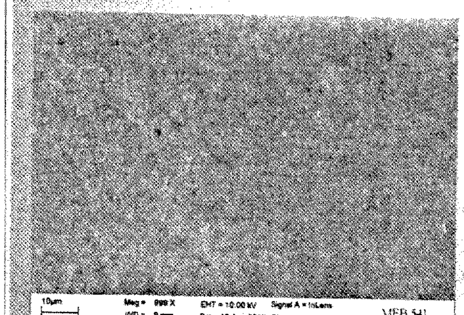
## MWCNT Samples (2 of 3)

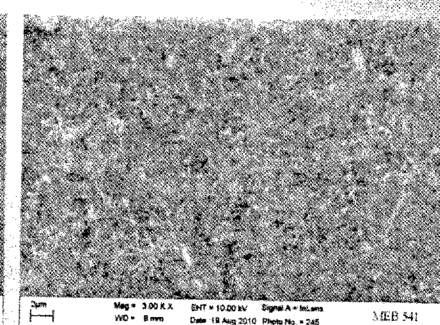
- Since the adhesion point of failure is at the catalyst/substrate level, we explored alternate substrate prep techniques
  - Explored Cr, Ti, and alumina thin film sticking layers under the Fe catalyst layer
    - Best results were achieved using the alumina thin film sticking layer
  - Sample: Enhanced adhesion MWCNTs on Silicon substrate



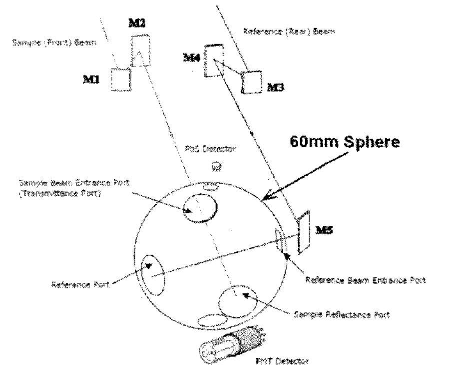
## MWCNT Samples (3 of 3)

- Because it is brittle, Si is not the material of choice for instrument components which control stray or scattered light, such as baffles or stops
  - Explored nanotube growth on materials capable of supporting higher structural loads, such as titanium, inconel, and alumina
  - Sample: MWCNTs on Ti substrate

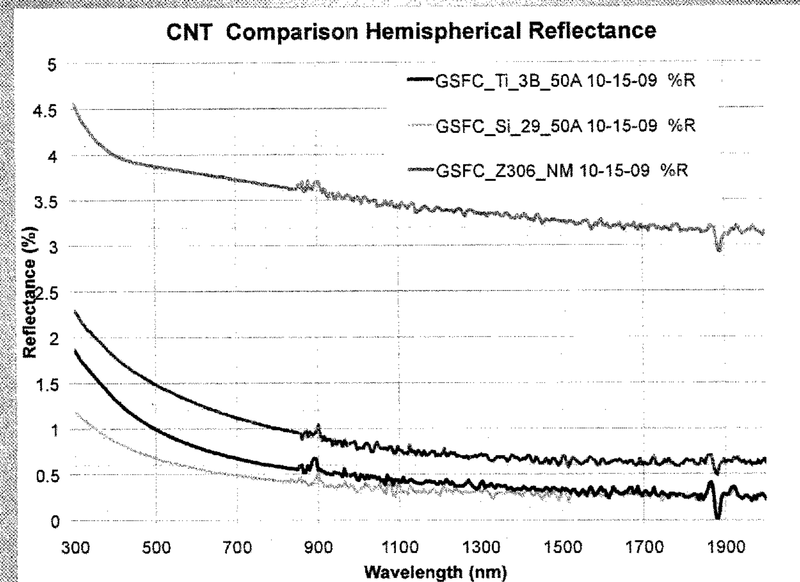




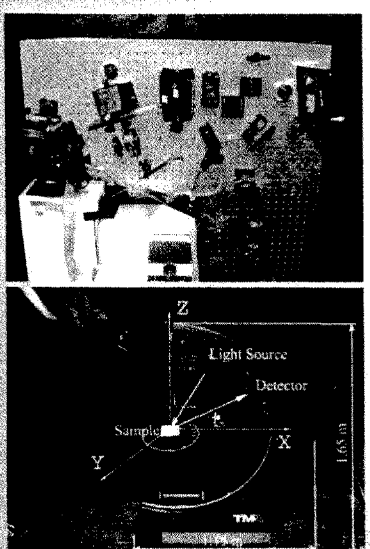
## Measurement of $8^0$ Directional/Hemispherical Reflectance

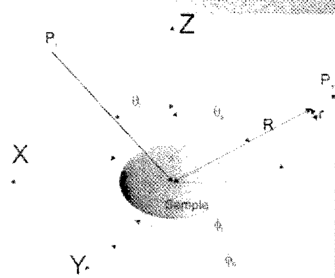



- MWCNT samples were measured for directional/ hemispherical reflectance using a PE Lambda 950 spectrophotometer from 300 to 2000 nm.




## Measurement of Bidirectional Reflectance Distribution Function (BRDF)



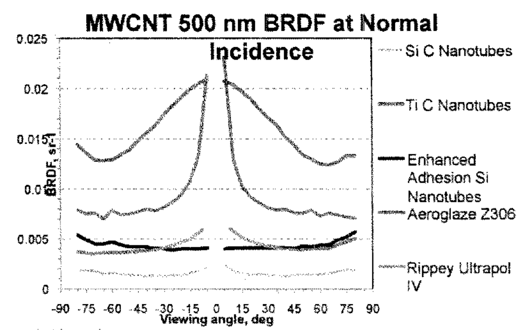




-BRDF:

$$BRDF = \frac{dL_r(\theta_i,\phi_i,\theta_r,\phi_r;E_i)}{dE_i(\theta_i,\phi_i)} = \frac{P_r/\Omega}{P_i\cos\theta_i}$$

-Initial measurements of BRDF made in-plane

- 500 nm and 900nm
- $0^0$ and $45^0$ incident
- $-80^0$ to $-80^0$ scatter

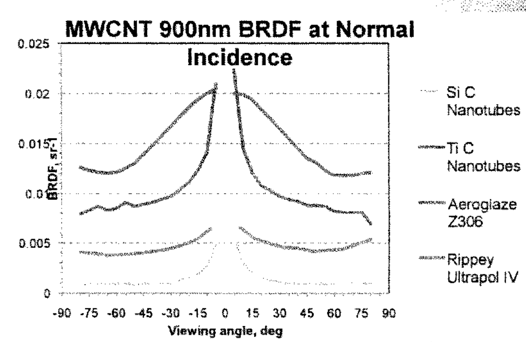


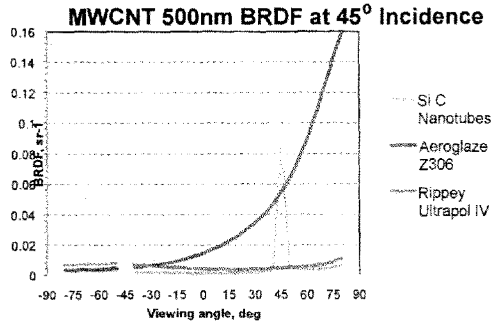

-Si C nanotubes exhibited the lowest BRDF values at normal incidence for 500 and 900nm illumination

-4 to 10x darker than Z306 paint
-2 to 4x darker than Ultrapol applique

-Enhanced adhesion Si nanotubes exhibited BRDF values comparable to Ultrapol at 500nm and 3 to 4x darker than Z306

-Ti C nanotubes exhibited higher BRDF values with a pronounced retroreflection



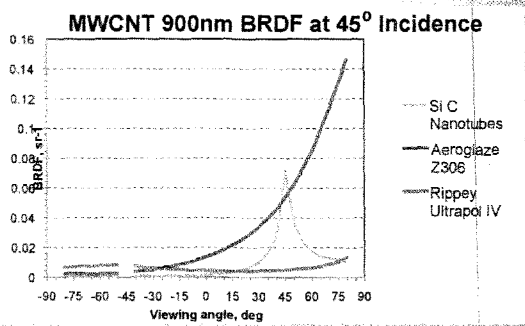



-Si C nanotubes exhibited a Significant specular reflectance peak

-This peak was sharper at 500nm
and wider at 900nm and exceeded
the Z306 specular peak

-Si C nanotubes exhibited negligible retroreflection at -45°

-At all non-specular angles, Si C
nanotubes exhibited lower BRDF
than Z306 and Ultrapol IV




## What is currently the "blackest ever black"?

**In BBC News: February 6, 2003**

**Blacker is the new black (NiP)**
British scientists say they have produced the "blackest ever" surface developed so far.
The industrial coating for telescopes is one of the darkest and least reflective surfaces on Earth.
By minimising the scatter of stray light, it could improve the vision of telescopes, from amateur instruments to the mighty Hubble.
It reflects 10 to 20 times less light than current coatings and has a number of applications in astronomy, such as on star trackers, which help spacecraft navigate.

"It's a very interesting surface to look at because it's so black."
Dr Richard Brown, NPL

**In Reuters: January 15, 2008**

**New material pushes the boundary of Blackness**Steenhuysen
CHICAGO | Tue Jan 15, 2008 6:30pm EST
CHICAGO (Reuters) - U.S. researchers said on Tuesday they have made the darkest material on Earth, a substance so black it absorbs more than 99.9 percent of light.
Made from tiny tubes of carbon standing on end, this material is almost 30 times darker than a carbon substance used by the U.S. National Institute of Standards and Technology as the current benchmark of blackness.

## In Conclusion

- Normally illuminated, MWCNTs on Si substrate are 3 to 10x darker at 500nm and 900nm than commonly used spaceflight qualified paint
- At 45° illumination, MWCNTs on Si substrate show a clear specular peak . Interestingly, no retroscatter was detected
- Enhanced adhesion MWCNTs produced a black surface with 1.4x to 1.0x the reflectance of the Si MWCNT surface.
- MWCNTs on Ti substrate produced a black surface with 2x the reflectance of the Si MWCNT surface
- A significant amount of testing is still required to qualify MWCNTs for space applications
  - Additional optical measurements: more wavelengths, incident angles, and scatter angles over full scattering hemisphere (currently underway)
  - Optical stability, uniformity, reproducibility (currently underway)
  - Mechanical stability: vibe, shock, aging tests
  - Thermal behavior
  - Chemical & physical stability: hygroscopic, out-gassing properties
  - Radiation stability
  - Electrical stability: on-orbit charging