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Infrared hemispherical reflectance of carbon nanotube mats and arrays in the 5–50 μm wavelength region ☆

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ABSTRACT

We present the absolute infrared (5–50 μm) hemispherical reflectance of films produced from commercially available carbon nanotubes. Spectra were obtained with the NPL directional-hemispherical reflectance measurement facility. One group of samples consisted of mats of carbon nanotubes sprayed on copper or silicon substrates. Another group consisted of vertically aligned carbon nanotubes grown on silicon. Two of the materials studied exhibited the lowest hemispherical reflectance so far observed in the infrared wavelength region.

Carbon nanotube (CNT) coatings have been reported as having very low reflectance throughout the visible and infrared spectrum [1,2], and are therefore attractive for applications that require high absorptance, such as coatings for thermal detectors, light baffles and optical instruments. CNTs are produced in very large quantities for industrial use in products such as plastics and paints and are no longer a laboratory curiosity. Therefore, we have investigated the optical properties of CNTs that are commercially produced and readily available. Yang and co-workers described a highly absorbing mat of nanotubes that was evaluated in the visible and near infrared [1]. Mizuno et al. have documented very low reflectance and high emittance of an array of nanotubes at wavelengths ranging from the visible to far infrared [2]. Lehman et al. first described the application of nanotubes on a thermal detector platform, and later showed that it is possible to achieve very low reflectance with additional processing steps for the pyroelectric detector platform [3]. Reports in the literature for hemispherical absolute reflectance at wavelengths longer than 20 μm or even 15 μm are rare. The facility and measurement techniques reported here are unique, and the characterization of materials with extremely low reflectance at or below the 0.01 level presented a challenge to the techniques and apparatus.

The samples were measured using the upgraded infrared directional-hemispherical reflectance facility at NPL. Measurement of hemispherical reflectance is usually carried out with an integrating sphere, which needs to have an internal surface that is a high reflectance Lambertian scatterer. Surfaces used in infrared integrating spheres become progressively more specular-like for wavelengths longer than about 20 μm. The NPL facility uses a hemispherical copper reflectometer that enables measurements to be carried out to wavelengths longer than 50 μm.

The operation of the NPL reflectometer is illustrated in Fig. 1. In the upper diagram of Fig. 1, radiation from the cylin-

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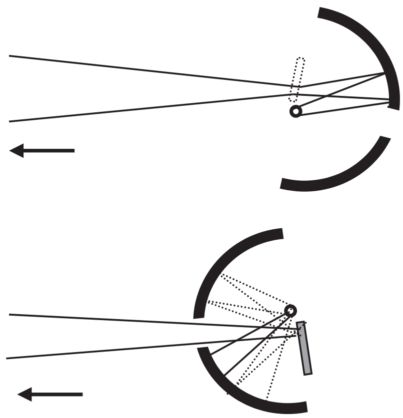

Fig. 1 – Operation of NPL hemispherical reflectometer. Plan view, with the direction of the spectrometer indicated by the arrows.

drical source is focused by the hemispherical reflector at the sample position (shown in dotted outline) and then travels onto the spectrometer for spectral analysis. This measures the radiance of the illuminated hemispherical mirror. In the lower diagram, the hemispherical mirror is rotated and the sample inserted and light from the hemispherical mirror which is reflected by the sample travels to the spectrometer. The ratio of the reflected radiance of the sample (lower) to the radiance of the irradiating hemisphere (upper) is numerically equal to the directional-hemispherical reflectance by the Helmholtz Reciprocity Principle – see [4] and references therein for further details.

The high radiance that illuminates the sample is a problem with absorptive samples, because the sample temperature can be raised, and the thermal radiation emitted by the sample can become significant for wavelengths longer than 10 μm. Sample heating cannot be eliminated by switching the source off, because the source gives rise to the wanted reflectance as well as the thermal radiation. A cylindrical (ideally spherical) source is required to illuminate the hemispherical reflector, which precludes the ability to spectrally filter or attenuate the radiation from the source. A process to minimize and correct for heating of the test samples was implemented in order to measure these and other highly absorptive samples [4]. The other significant improvement recently introduced was to use of a Fourier-transform infrared (FTIR) spectrometer instead of a grating spectrometer to generate spectrally resolved data. The facility covers wavelengths from 2.5 μm to 50 μm and uses all-reflective optics, apart from the spectrometer beamsplitters and the windows that seal the pyroelectric detectors.

Two types of “sprayed” multiwall carbon nanotube (MWCNT) black coatings were investigated. One was based on MWCNTs, and the other on MWCNTs surrounded by a shell of boron-doped silicon carbon nitride (BSiCN). The MWCNTs were produced commercially by Nanocyl[1] and are described by the manufacturer as having greater than 96% CNT content and being approximately 10 nm in diameter. In addition, this material is sold as being -COOH functionalized to facilitate dispersion and mixing. The BSiCN surrounding the MWCNTs is a polymer derived ceramic, similar to that described elsewhere [5]. In the first instance, the Nanocyl mat was sprayed from solution containing 100 mg of nanotube-based material, 20 ml distilled water, 0.5 mg dodecylbenzensulfonic acid (DBS) and 0.5 ml potassium silicate solution. The BSiCN/MWCNT dispersion is identical, but without potassium silicate. The DBS functions as a surfactant for uniform dispersion of the nanotubes; while the potassium silicate is a ceramic binder. The topology of the sprayed coatings was observed by means of scanning electron microscope (SEM) and appears as a dense mat of nanotubes with small or non-existent air interstices.

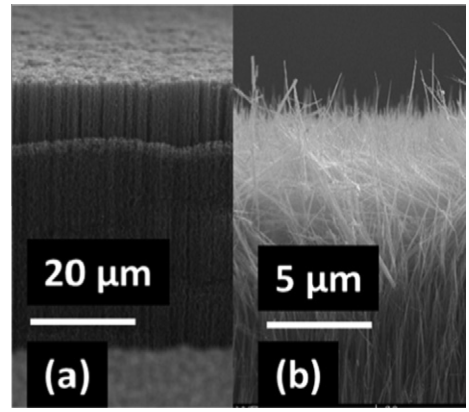

Fig. 2 – SEM image (side view) of VANTAs from (a) FirstNano, (b) Nanolab.

Two types of vertically aligned CNT array (VANTA) coatings were investigated. The first VANTA was grown by FirstNano[1] by use of water-assisted chemical vapour deposition (CVD) at 750 °C with ethylene. To facilitate the growth of 160 μm long MWCNTs, a 20 nm aluminium buffer layer and 2 nm iron catalyst were deposited on top of a Si substrate. The second type of VANTA coating was grown by Nanolab[1] on Si substrates by plasma enhanced chemical vapour deposition (PECVD). The substrate was coated with a metal catalyst layer consisting of a 300 nm thick chromium layer, (purity 99.99%) and then a 10–50 nm thick nickel layer (purity 99.99%). The growth of 40 μm long nanotubes from PECVD was accomplished by the introduction of acetylene gas while powering the plasma source at 0.47 A. The length, diameter and site density of the carbon nanotube arrays were verified by means of SEM, see Fig. 2.

Fig. 3 shows the hemispherical reflectance of four of the test samples at temperatures of 15 °C. The peak near 10 μm for the nCylSi sample is due to silicate. The VANTA samples show reflectances of 0.0035 ± 0.003 up to 10 μm, and then show a slight trend upwards to about 0.010 ± 0.006 by 50 μm. The increase in the uncertainties for wavelengths longer than 10 μm is due to the uncertainty introduced in correcting for heating effects, as well as the rapidly deteriorating signal-to-noise levels.

[1] Trade names are identified only for reference purposes and do not represent or imply an endorsement by the authors.

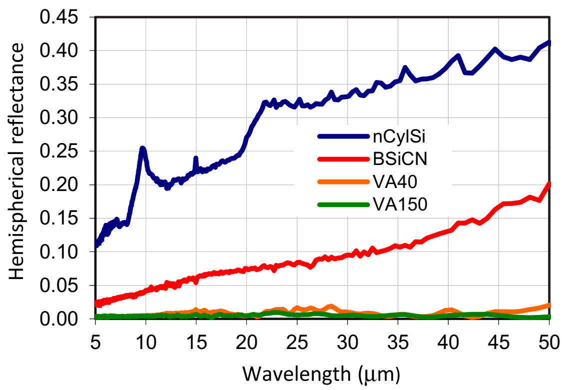

Fig. 3 – Hemispherical reflectance of MWCNT samples from 5 μm to 50 μm.

The VANTA samples appear to be *the blackest materials so far observed*, based on a survey of the literature. The condition of *hemispherical* rather than merely specular reflectance limits the search. We considered reports that were: (1) truly of hemispherical reflectance; (2) comparably low with any reported uncertainty. In the first case, Betts et al. examined the hemispherical reflectance of several black coating materials at wavelengths from 2.5 μm to 50 μm, with the lowest reflectance monotonically increasing to 0.1 from 2.5 μm to 50 μm [6]. In the second case, Becker et al. examined reflectance from 17 μm to 1000 μm for gold-black coatings, the value of at least one sample being comparable at less than 0.03 [7]. Our results corroborate the findings of Mizuno et al. [8] for water-assisted CVD grown VANTAs. In light of Betts et al. [9] Becker et al. [7] Mizuno et al. [8] and modelling by Theocharous et al. [10], we attribute the infrared properties of the coating to several factors. In the first place, graphitic carbon has intrinsically low reflectance. The VANTA may be considered a composite consisting of a low-reflectance material and air. Therefore, it is an effective medium with a topology that presents a porous structure and multiple opportunities for photons to be absorbed. Shi et al. quantify the index of a very black VANTA to be only slightly greater than that of air. That is, the index of the VANTA in air is near unity (the imaginary component being much less than unity). [11] Compared to the VANTA, the sprayed coatings from either bulk MWCNTs or BSiCN/MWCNT are denser and less porous (more graphitic carbon and less air per volume) and therefore have higher reflectance.

It is clear that commercially available carbon nanotube arrays exhibit extremely low reflectance in the infrared. Although such materials are readily available, the challenge remains to make such coatings commonplace on shapes and materials other than planar silicon. The way forward points to applications such as infrared blackbodies, greatly reduced scattered light in instrumentation, and thermal detectors with broad and uniform responsivity.

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