

High-Efficiency Optical Absorbers Derived from Carbon Nanostructures

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ABSTRACT

Optical absorbers based on vertically aligned multi-walled carbon nanotubes (MWCNTs), synthesized using electric-field assisted growth, are described here that show an ultra-low reflectance, 100X lower compared to the benchmark, a diffuse metal black - Au-black - from wavelength $\lambda \sim 350 \text{ nm} - 2500 \text{ nm}$. The reflectance of the MWCNT arrays was measured to be as low as 0.02 % at 2 μm . The choice of the starting substrate was deemed to be particularly important in order to synthesize a high-areal density of the MWCNTs using the plasma-based chemical vapor deposition (CVD) process which directly impacts the optical absorption efficiency of the nanoabsorbers. Such high efficiency absorbers are particularly attractive for radiometry, as well as energy harnessing applications.

Keywords: carbon nanomaterials, optical absorbers, nanoabsorbers, MWCNTs, PECVD

1 INTRODUCTION

The ability of nanomaterials to trap light effectively has important implications for their use in energy harnessing, optical blacks for radiometry, as well as detectors. A survey of a host of nanomaterials, such as CdSe nanocrystals [1], graphene [2], and graphene quantum dots [3], reveals the promise such materials have in a wide range of optical applications. In this paper, we report on another type of nanomaterial which is exceptional at trapping incoming light as a result of its unique physical structure, a structure comprised of porous arrays of thin (10-15 nm diameter) vertically oriented multi-walled carbon nanotubes (MWCNTs). By virtue of the photo-thermal transduction mechanism, such CNT absorbers have promise in energy harnessing, high sensitivity thermal detectors, and in serving as a reference for quantifying absolute optical power in optoelectronics. Other potential applications include their use in radiative cooling, thermography, antireflection coatings, and optical baffles to reduce scattering.

Porosity in ordered nanostructures has been theoretically [4] shown to enhance optical absorption

properties, which has also been verified experimentally in Si-based nanomaterials [5,6], and similar conclusions have also been drawn from theoretical calculations made on low-density arrays of CNTs [7]. Experimentally, the ultra-low reflectance properties arising from MWCNT arrays was recently demonstrated by Yang *et al.* [8], and Mizuno *et al.* [9], conducted emissivity measurements on forests comprised of single-walled carbon nanotubes (SWCNTs) into the infrared (IR). While earlier reports on the optical response from arrays of MWCNTs [8] were primarily conducted in the visible ($\lambda \sim 450\text{-}650 \text{ nm}$), in this paper we demonstrate the ultra-low reflection properties of MWCNT ensembles into the IR regime, where the optical performance of traditional black materials, such as black paint or graphite, degrade considerably. The previously synthesized MWCNTs [8] and SWNTs [9] for optical absorber applications were formed using water-assisted thermal chemical vapor deposition (CVD), which yields CNT lengths in excess of 100's of microns. Vertical alignment, deemed to be a critical feature in enabling the high optical absorption from CNT arrays, occurs primarily via the crowding effect [10,11] with thermal CVD synthesized CNTs, which is generally not effective in aligning CNTs with lengths $< 10 \mu\text{m}$. Here we show for the first time that the electric field inherent in a dc glow discharge yields vertically aligned CNTs at small length scales ($< 10 \mu\text{m}$), which still exhibit broadband, and high-efficiency optical absorption characteristics from the ultraviolet (UV)-to- IR.

2 APPLICATIONS AND EXPERIMENTAL

In Section 2.1 we provide an example of the use of black materials in radiometry applications for space-based systems, followed in Section 2.2 with a description of the synthesis of these materials using plasma enhanced (PE) CVD. Then in Section 2.3, a comparison of the optical properties of the nanoabsorber is provided with respect to a benchmark black material. Finally, the effect of the plasma power on the vertical alignment of the MWCNTs is discussed in Section 2.4.

2.1 Radiometry Applications

The blackness of a material directly impacts its utility in a wide variety of applications. One such example is their use in space based systems for radiometry applications. Shown in Fig. 1 (top) is the Mars Reconnaissance Orbiter (MRO) launched by NASA in 2005. An instrument on MRO is the Mars Climate Sounder (MCS) (bottom of Fig. 1) which performs climatic investigations of the Martian atmosphere, including compositional analysis. One feature of MCS is the presence of a blackbody calibration target whose blackness directly impacts the sensitivity and accuracy of the spectra gathered by such a sounder. Although cavity black-bodies are used, they are physically large and massive, and thus there is a motivation to engineer materials that are inherently absorbing for serving as a reference, which would reduce the payload by decreasing the mass and volume.

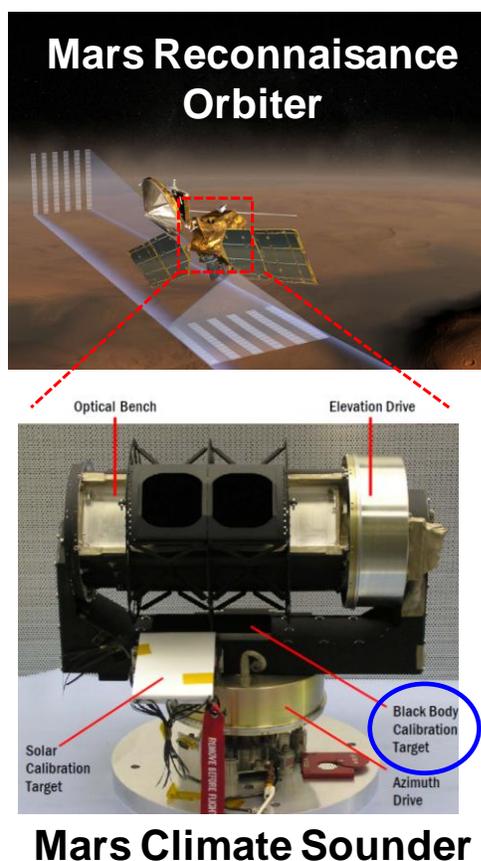


Figure 1. The Mars Reconnaissance Orbiter (MRO) launched by NASA in 2005 (top). The Mars Climate Sounder (MCS) is an instrument on MRO (shown at bottom). One purpose of MCS is to perform compositional analysis of the Martian atmosphere. MCS has a blackbody calibration target for serving as a reference and the blackness of this target directly impacts the accuracy and sensitivity of the spectra gathered by the sounder.

2.2 Synthesis

We have explored the use of CNTs synthesized using PECVD for the formation of a nanoabsorber which is inherently absorbing over a broad spectral range from the UV-to-IR. The choice of the starting substrate was deemed to be particularly important for synthesizing a high areal density of MWCNTs. For example, the SEM image in Fig. 2a shows amorphous carbon deposits when the Co catalyst was placed directly on Si at 750°C; the optical image on the right of Fig. 2a shows a largely reflective surface. On the other hand, with the right choice of buffer layer, the sample appeared visually black (right inset of Fig. 2b). Inspection of this sample in the scanning-electron-microscope (SEM) revealed a high areal density of CNTs, as shown in Fig. 2b, that help to trap incoming light and suppress reflection, causing the sample to appear visually black.

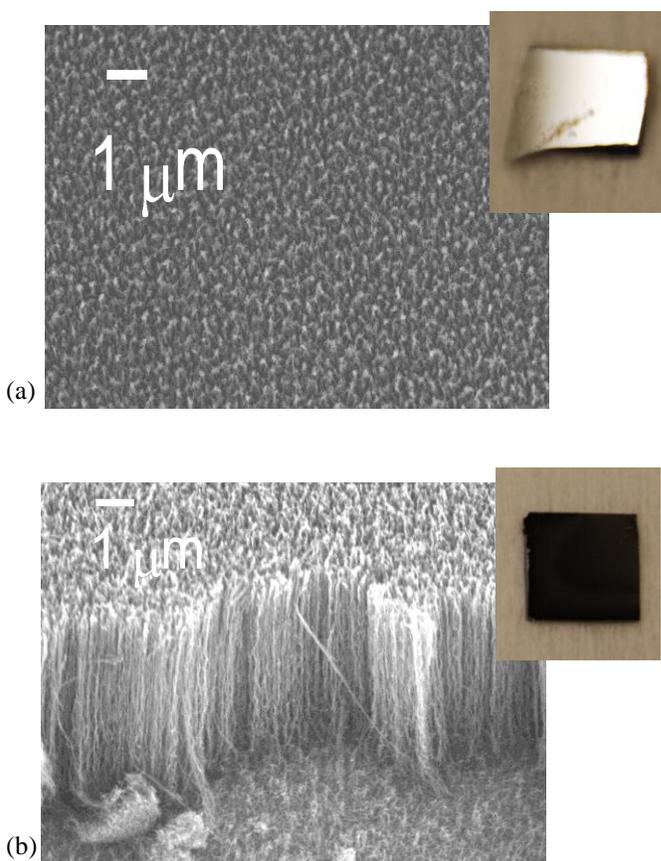


Figure 2. (a) SEM micrograph of growth resulting with dc PECVD when the catalyst was placed directly on Si; inset shows an optical image of the sample depicting a predominantly reflective surface; (b) SEM micrograph depicts a high areal density of CNTs with the right choice of buffer layer on Si; inset shows an optical image depicting a visually black sample. The spatial uniformity of the CNTs appears good over large length scales.

2.3 Comparison to Benchmark

The optical reflectance response for the CNT absorber film was compared to a standard optical black, Au-black absorber sample, which was synthesized using approaches similar to prior reports [12]. The SEM micrograph in Fig. 3a reveals the percolated structure comprising of random networks in the porous Au-black sample, quite unlike the highly aligned MWCNTs in our absorber arrays (Fig. 3b).

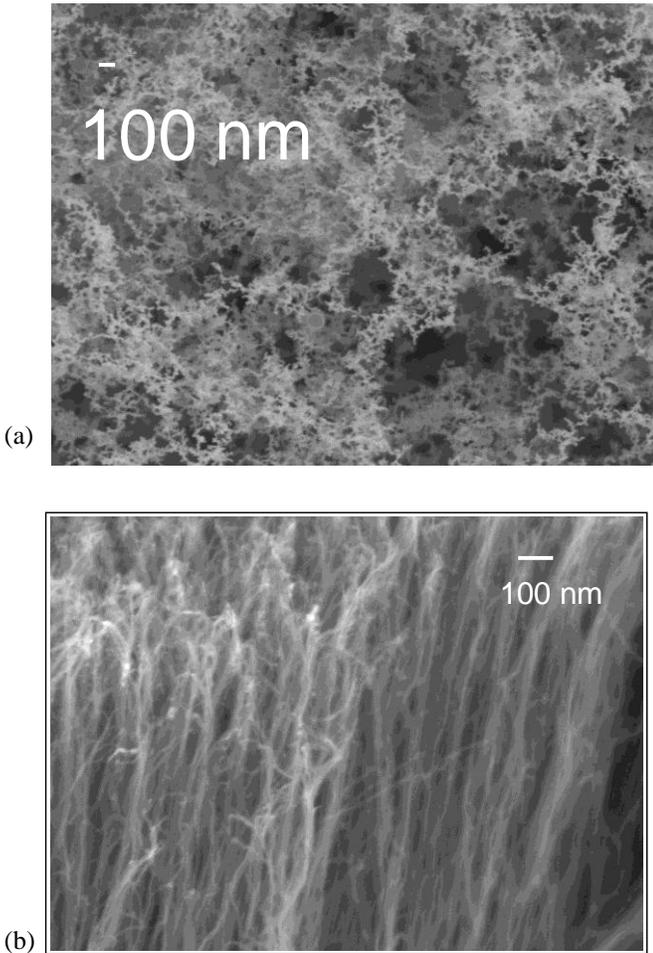


Figure 3. (a) An SEM micrograph of the benchmark, a diffuse metal-black, Au-black absorber sample (taken at 30° viewing angle). The Au-black is comprised of a percolated, randomly aligned network of fibers. This is unlike the vertically aligned structure of the MWCNT arrays as shown in the high magnification SEM image in (b). The porous structure is comprised of a rough and non-continuous surface with MWCNT diameters in the 10-15 nm range.

The optical measurements on the samples were conducted from $\lambda \sim 350$ nm to 2500 nm. The measurement system comprised of a high resolution, fiber coupled, spectroradiometer (ASD inc, Fieldspec Pro) where a standard halogen light beam was aimed at normal incidence to the sample, as shown by the schematic in Fig. 4. The

bare fiber connector of the spectroradiometer was oriented at $\sim 40^\circ$ from the normal. Relative reflectance spectra were obtained by first white referencing the spectroradiometer to a 99.99 % reflective spectralon panel. The reflected light intensity from the sample under test was then measured and the spectra were compared for samples synthesized at different growth conditions.

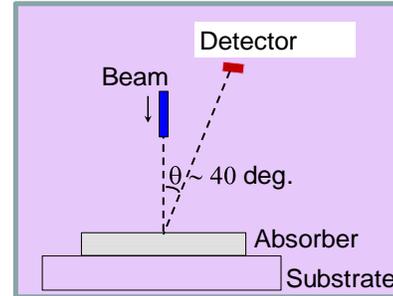


Figure 4. A schematic of the measurement set-up.

Figure 5 depicts the reflectance spectra of the nanoabsorber and compares the response to the Au-black absorber sample. The reflectance of the CNT absorber is nearly 100 X lower than that of the Au-black absorber sample, ~ 0.02 % at $\lambda \sim 2$ μm , compared to 1.1 % for Au-black. Other families of absorbers, such as NiP with micro-scale surface asperities, have higher reflectance $\sim 0.5 - 1$ % for $\lambda \sim 320 - 2140$ nm [13], while ultra-black NiP alloy has a reflectance $\sim 0.16 - 0.18$ % from $\lambda \sim 488 - 1500$ nm [14]; black paint has a reflectance > 2.5 % from $\lambda \sim 600 - 1600$ nm. It should also be noted that the spectra obtained for the MWCNT absorber is wavelength independent in the 350 - 2500 nm spectral range unlike the Au-black sample which has a wavelength dependent response, as Fig. 5 indicates.

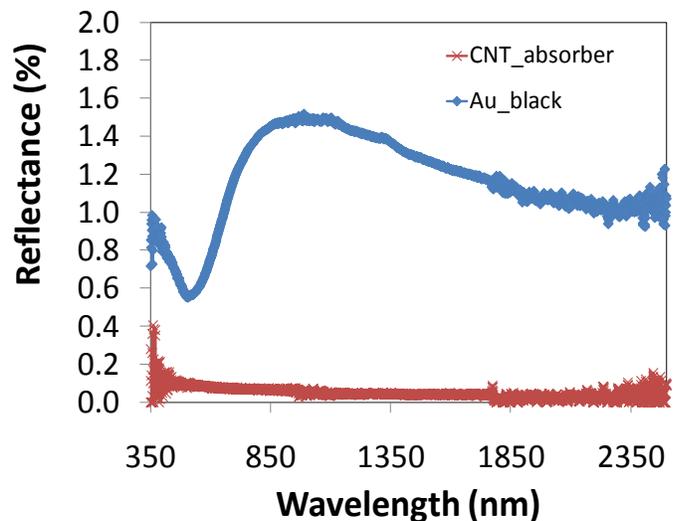


Figure 5. Reflectance measurement from $\lambda \sim 350$ nm - 2500 nm for the MWCNT absorber synthesized using dc PECVD and a Au-black absorber sample. The Au-black reference sample has a reflectance that is nearly ~ 100 X larger than our CNT absorbers, ~ 0.02 % at $\lambda \sim 2$ μm compared to 1.1 % for Au-black.

2.4 Plasma Power

Vertical alignment appears to be a critical feature in enabling the exceptional optical absorption properties from the CNT forests [8,9]. Unlike in thermal CVD where vertical alignment occurs via the crowding effect [10,11] in ultra-long CNTs (e.g. > 400 μm in Ref. 8), with dc PECVD alignment occurs as a result of the E-field in the glow discharge, enabling MWCNTs with lengths < 10 μm to be relatively well-aligned. To examine the impact of the E-field on CNT characteristics, the plasma power was adjusted. As shown by the SEM images in Fig. 6a, at a plasma power of ~ 120 W, the synthesized CNTs were not well aligned and the corresponding reflectance from such films was higher. However, as the plasma power was increased to ~ 170 W, the degree of alignment increased, as the SEM image in Fig. 6b indicates. The sample synthesized at 170W of plasma power appeared visually black. The impact of vertical alignment on the optical characteristics is also obvious in other nanostructured films where disordered Si NW mats exhibit a yellow or brown appearance since most of the light is reflected by scattering [15], while ordered Si NWs appear visually black and suppress reflection [16].

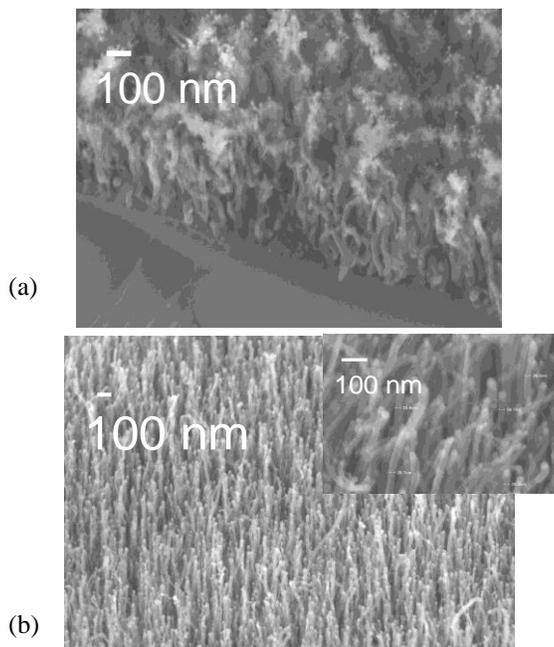


Figure 6. Effect of the plasma power on growth characteristics. a) Growth at 120 W of plasma power showing tubes are randomly oriented and the growth seems to be suppressed. b) SEM micrograph of a sample synthesized at the same growth conditions where the plasma power was increased to 170 W where the CNTs appeared more vertically aligned. The bottom sample appeared visually black.

In conclusion, we have successfully shown that dc PECVD synthesized MWCNTs exhibit ultra-low

reflectance properties over a wide spectral range from UV-to-IR for relatively thin (< 10 μm) absorber ensembles. The structural characteristics of the MWCNT absorbers were engineered by controlling the bottom-up synthesis parameters during PECVD which enabled optimization of the optical properties of the nanoabsorbers.

3 ACKNOWLEDGEMENTS

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