Enhancement of Optical Absorption by Oxygen Plasma Treatment in Carbon Nanotube-based Black Paint Coating

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Abstract: The effect of oxygen (O_2) plasma treatment on the reflectance properties and surface morphology of carbon nanotube-based paint was investigated. We demonstrate a hemispherical reflectance of less than 2.5% throughout the UV-Vis-NIR range.

1. Introduction

Broadband light absorbers show great potential for various applications like efficient absorbers/emitters for energy conversion, infrared thermal detectors, and stray-light elimination [1]. Carbon nanotube (CNT)-based coatings are appealing for broadband and uniform absorption due to their low broadband reflectivity as well as mechanical, and thermal properties [2]. However, their scalability is hindered for complex structures by fabrication using chemical vapor deposition and subsequent transfer, complications of high temperature (~ 700 °C) growth, as well as structural anisotropy that causes angle selective absorption. Considering these limitations, there is a recent trend of developing CNT-based black paints by dispersing CNTs in a solution containing primarily a surfactant, crosslinking agent, and a polymer. This process allows scalable deposition of CNTs that is compatible with industrial requirements and offers high broadband absorption without angular dependency and is shape-independent. The optical properties of these paints can be improved further by oxygen (O_2) plasma treatment for surface modification and functional group optimization, which further enhances broadband absorption. O_2 plasma treatment has the advantage of a short reaction time, uniform functionalization, and allows for fine-tuning of properties, thereby, allowing large-scale production. Within this concept, we have studied the absorption properties of a scalable CNT-based paint across ultraviolet-visible-near infrared (UV–Vis–NIR) to far infrared range (FIR) range. The reflectance and morphology of the paint have been investigated after various O_2 plasma treatments.

2. Experimental

The paint coating was prepared on a cleaned and etched aluminum substrate. First, the substrate was spray-coated with a primer and cured at 150 °C for 24 h. Then, a commercial black paint of thickness ~ 125 µm was sprayed on the primer-coated substrate and baked at 150 °C for 24 h. O_2 plasma treatment was performed for five consecutive times at 5×10^{-4} bar in an asher equipped with an RF generator at 50 W and an O_2 flow rate of 50 sccm. Reflectance and morphology were observed between each O_2 plasma treatment. The reflectance spectra from 0.25 µm to 2.5 µm were recorded by a commercial UV–Vis–NIR spectrophotometer. The specular reflectance was measured at an incidence angle of 65°. The hemispherical reflectance spectra of the sample were recorded at 8° using an integrating sphere calibrated with a NIST-traceable standard black reference material. The discontinuity in the data around 0.395 µm and 1.505 µm – 1.545 µm is due to a change in measurement configuration for the reference material. Fourier transform spectroscopy (FTS) measurements were collected using an integrating sphere with 100 cm^{-1} resolution in the range of 1 – 18 µm and normalized to a NIST-calibrated diffuse gold sample. A scanning electron microscope (SEM) was used for observing surface morphology.

3. Results

Figures 1a and 1b show the specular and hemispherical reflectance spectra in the UV–Vis–NIR. Regardless of specular or hemispherical measurements, the reflectance decreases with increasing exposure time under O_2 plasma treatment. The diffuse reflectance is higher than the specular reflectance. For the sample plasma treated five times, the specular reflectance is less than 0.10% and hemispherical reflectance is less than 2.5% throughout the UV–Vis–NIR range, indicating that the paint is highly absorptive in that range. As a consequence of the plasma treatment, reflectance minima shift towards longer wavelengths. **Figure 1c** represents hemispherical reflectance in the entire wavelength range from 0.25 µm – 18 µm. The sample, plasma treated five times, shows hemispherical reflectance of greater than 8% from 9.5 µm – 18 µm. The high reflectance in the FIR range is due to the dominant reflectance properties of the underlying Al substrate. The absorption of the paint can be increased in the FIR range by increasing the thickness of the paint.

To determine the reason for the optical properties, the surface morphology of the as-deposited coating was compared with that of the 260 s plasma-treated sample. The untreated film has a random network structure of CNTs, as shown in **Figure 1d**. After 260 s of plasma treatments, the coating showed a porous and rough morphology in **Figure 1e**. During the plasma treatment process, electrons, ions, and UV light interact with the surface, leading to breakage of C=C bonds and creating active sites for the functionalization of oxygen to form C-O-C, C-O, O-C=O bonds [3]. As a result, chemical and physical modifications are introduced in CNT paint. When optical radiation is incident on the porous surface, multiple reflections occur which increase light interaction with the CNTs, thereby, results into increased absorptance. Hence, changed chemical bonds and porous morphology are important for maximum absorption in CNT-based paint.

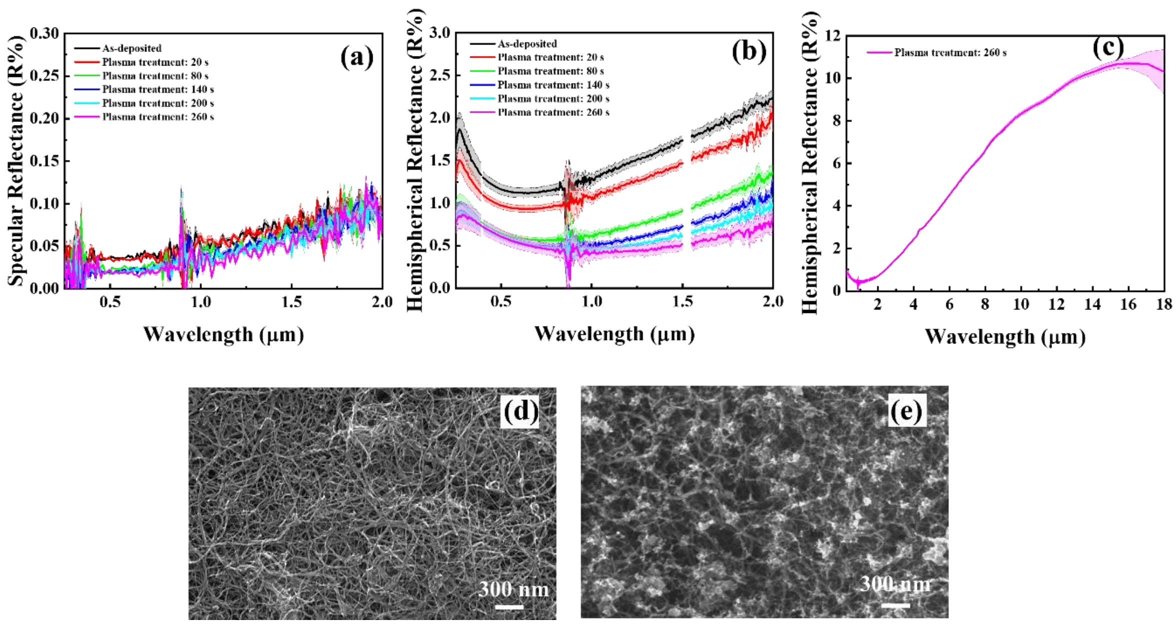

Figure 1: (a) Specular and (b) hemispherical reflectance of as-deposited and plasma-treated sample (0.25 μm – 2 μm), (c) hemispherical reflectance in 0.25 μm – 18 μm range after 260 s of O_2 plasma treatment. Uncertainty is shown by shading; Surface morphology of (d) as-deposited and (e) 260 s plasma-treated sample.

4. Conclusion

CNT-based paint was developed using a spray coating method and was treated in an O_2 plasma environment to enhance absorption over a broad wavelength range (0.25 μm – 18 μm). The spray-coated CNT paint on Al substrate is promising as an absorber, particularly in UV–Vis–NIR range. However, the reflectance increased in FIR range due to the Al substrate. These results show that the readily scalable CNT-based paint can be applied to commercial products with absorption comparable to other coatings [4]. By increasing the thickness to improve the FIR absorption further, the O_2 plasma-treated CNT paint can be potentially used as a broadband absorber for larger-scale applications.

5. Acknowledgments

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6. References

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