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Wet deposition of carbon nanotube black coatings for stray light reduction in optical systems

Suzanna Azoubel [a], Rina Cohen [b], Shlomo Magdassi [a,*]

[a] Casali Institute of Applied Chemistry, Institute of Chemistry, The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel
[b] Elbit Systems Electro-optics (Elop), Advanced Technology Park, POB 1165, Rehovot 76111, Israel

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ABSTRACT

Stray light, also known as optical noise, affects the performance of many optical devices. It can be reduced to a tolerable level by well-designed and well-baffled system or/and by using functional black coatings that are fabricated in a complex and costly process. Carbon nanotubes (CNTs) absorb light strongly, making them an ideal candidate for realizing a super black coating. CNT coatings were formed by spraying formulations composed of a silicon binder and low cost multiwalled CNTs on a pre-heated aluminum plate. The diffuse reflectance of the coatings in the VIS range (350–800 nm) was in the range of 2.6–5.11%, depending on the MWCNT concentration in the coating. In the NIR range (850–2400 nm), the reflectance values were in the range of 4–6.5%, however the dependence on MWCNT concentration was not very significant. Excellent adhesion to the aluminum substrates was achieved, for coatings with CNT concentration below 15%, while still having very low reflectance, even at temperature cycling between 200 °C and −196 °C. The proposed coating formulations enable simple and low cost approach for producing high light-absorbing coating of complex 3D structures within a very short time by wet deposition of CNTs.

1. Introduction

The performance of optical devices, regardless of their complexity, has always been affected by stray light, which can also be called “optical noise”. The effect of stray light in optical systems may vary from causing low performance (reduced contrast on the image plane, obscure faint signals or false ones, false artifacts across the image plane, and magnitude errors in radiometric measurements) to physical damage (damaging fragile optical components and burning out detectors) [1,2].

Stray light can never be totally eliminated, however, it can often be reduced to a level at which it is tolerable. Just as electrical or acoustical noise can be reduced, so can optical noise, by proper design of the mechanical system [3–6] or/and by using functional black coatings in elements of the optical system [7–10].

A functional optical absorbing coating can be made of an ideal black material which is capable of absorbing light perfectly, at all angles and over all wavelengths. Common methods for producing such coatings are anodizing the metal with an inorganic black coloring process [8, 11–14] and electroless deposition of nickel oxide coating [9,15–17]. Both methods are time consuming and require several process steps, such as substrate surface pre-treatment.

Carbon nanotubes (CNTs), are known as excellent light absorbers, especially when grown as vertically aligned forests [18-20], and therefore they are ideal candidates for realizing a super black coating.

A CNT forest (aligned dense nanotubes placed perpendicularly to the surface) has been reported as optical coating [20–22], and as NASA announced, these coatings are “blacker than the blackest black”. Although this type of coating shows excellent light absorption and anti-reflective performance, its production requires unique equipment and specific conditions, since the CNT forest, is usually grown by chemical vapor deposition process (CVD) under high temperature and pressure. This is a high cost process and has additional drawbacks, such as the limited coating area and substrate type, and poor adhesion to the substrate.

The objective of the present report is the formation of a non-reflective, high light-absorbing coating, by a wet deposition process based on using a multiwalled CNT low-cost ink. This coating is performed by conventional air spraying process, is suitable for rapid coverage of large areas of various substrates. The resulting coatings are suitable for stray light absorption in optical devices, can be easily performed for complex 3D structures, and due to their excellent adhesion are suitable for use in space or terrestrial applications.

2. Materials and methods

The following two multi-walled carbon nanotube (MWCNT) formulations were used in the coating formulations: Baytubes® C70 P (Bayer

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* Corresponding author. Tel.: +972 2 6584967; fax: +972 2 6584350.
E-mail address: magdassi@mail.huji.ac.il (S. Magdassi).

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MaterialScience, Germany) characterized by a purity of >99%, a diameter of 13–16 nm and a length of 1–10 μm and NC7000 (Nanocyl, Belgium) characterized by a purity of >90%, a diameter of 9.6 nm and a length of 0.5–2 μm. The starting coating formulations were composed of MWCNTs (0.5 wt.%), dispersing additive BYK 9077 (1 wt.%) (Byk-Chemie GmbH, Germany), and dimethylformamide (DMF) (98.5 wt.%) (Biolab, Israel). The formulations were prepared using a horn sonicator (model Vibra-Cell, Sonics & Materials Inc., USA) for 20 min at 640 W. The samples were cooled in an ice water bath during the sonication process. This starting formulation was mixed at various ratios with a silicon-based binder. A binder solution was prepared by dissolving SILRES® REN 168 (0.5 wt.%) (Waker Chemie AG, Germany) in DMF. The final coating formulation was prepared by mixing the MWCNT dispersion and the binder solution at several ratios. The substrates and aluminum plates (1 mm × 50 mm × 50 mm size) were degreased by sonication in an acetone bath for 5 min. The coatings were formed by airbrush spraying 20 g of the coating solution onto heated aluminum plates (70 °C). The coated samples were further baked at 350 °C for 120 min.

The binder curing process was studied by TGA–MS analysis (40–350 °C, in a heating rate of 10 °C/min), using a STA TG–DSC 449 F3 Jupiter® instrument (NETZSCH, USA).

The diffuse reflectance of the coatings was measured in the VIS–NIR range (350–2400 nm) using a Cary 5000 spectrophotometer instrument (Varian, USA). Coating thickness was measured using a micro-TRI-gloss μ instrument (BYK Gardner GmbH, Germany). Adhesion test was performed according to standards ASTM D 3359 and ISO 2409 by using a Cross-Cut-Tester (1 mm) (BYK Additives & Instruments, Germany). In this test, a lattice pattern is cut into the coating penetrating through the substrate. A tape is placed on the cut pattern and then pealed. The adhesion is rated based on observing the un-peeled coating area, in accordance with the standard scale. Coating morphology was observed using High Resolution SEM Sirion and stereo microscope SQF II (China).

3. Results

Black coatings were formed by spraying a constant amount of the coating formulation on an aluminum plate pre-heated at 70–100 °C. The performance of the resulting coatings was evaluated by measuring the light reflectance (%R) in the range of 350–2400 nm. To ensure a good adhesion of the black coating to the aluminum substrate, each formulation contains, in addition to the MWCNT as the absorbing material, a heat resistant binder, at various weight ratios. The evaluation of the effect of MWCNT:binder ratio was performed with coatings with a similar thickness, 2–3 μm. The measurements were also conducted for a formulation without a binder, and for a formulation with a binder only. After performing the spray coating, the resulting wet coatings were dried to evaporate the solvent, followed by baking at 350 °C for 2 h, to convert the binder into a ceramic matrix. The coating morphologies before and after baking are shown in Figs. 1 and 2. As seen, prior to the thermal treatment there is a layer of the organic binder on top of the CNTs, while after baking this layer is partly removed, clearly showing the presence of entangled MWCNTs.

The thermal process for the binder curing process was studied by TGA–MS analysis. The binder material consists of siloxane chains with silanol end groups. During heating, the siloxane chains are cross linked by the condensation of –OH groups (releasing H_2O). It was found (Fig. 3) that the curing process starts at 200 °C. At this temperature, as found by the MS, the decrease in the mass is due to the release of the –OH fragments and H_2O molecules.

3.1. Optical properties of coatings

The reflectance of the coatings obtained by spraying was measured at the VIS–NIR range, and is presented as a function of wavelength (Figs. 4 and 5), and also as the calculated integral of reflectance ($\%R_{1,2}$) at each range: $\%R_1$ for 350–800 nm and $\%R_2$ for 850–2400 nm (Table 1). The coating experiments were conducted with two types of CNTs, 1–10 μm long, Baytubes® C70 P (BT), and 0.5–1.5 μm long, Nanocyl 7000 (NC).

In the VIS range (350–800 nm) aluminum plates have the integral of reflectance $\%R_1 = 59.87(\pm 3.35)\%$. After coating the substrate with the binder solution without CNTs, the reflectance slightly decreases up to $\%R_1 = 45.79(\pm 10.98)\%$. The reflectance decreases significantly while using the coating formulations with the two types of MWCNTs: Coatings composed of 7% MWCNT/binder 93% has $\%R_1 = 5.11(\pm 0.04)\%$ (for BT type) and $\%R_1 = 5.05(\pm 0.04)\%$ (for NC type). A further decrease of $\%R_1$ was found, as the concentration of the MWCNT in the coating increased, reaching a minimum value of $\%R_1 = 2.60(\pm 0.01)\%$ for BT

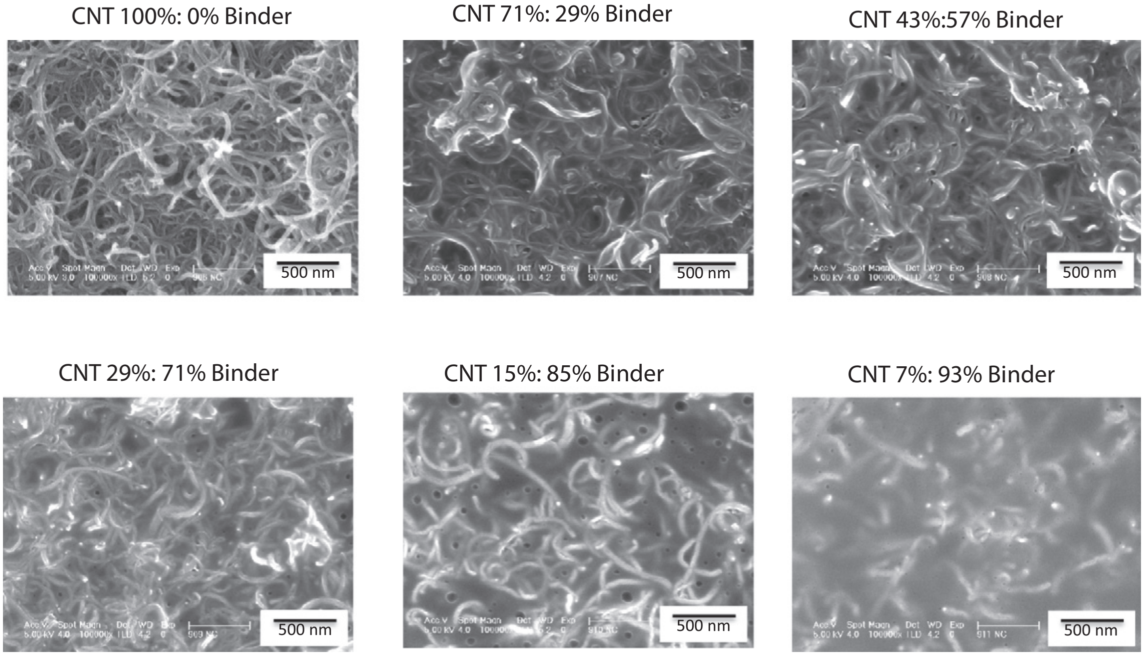

Fig. 1. SEM images of different BT/binder coatings, before curing.