ABSTRACT

Black coatings with high light absorptivity are of great importance for many applications. It is concluded that the morphology of the coatings can greatly affect the absorptivity. Here, the influence of the morphology in controlling the light absorptivity of carbon nanotube composite coating has been studied. Carbon nanotube composite films are fabricated by painting carbon nanotube-cyanoacrylate slurry on the substrate. Uniform micro-cones on the surface of the coatings were fabricated by laser irradiation in air. The angles of the microcones obtained could be controlled by changing the energy density of the laser pulses. The spectral absorptivity measurement from 0.25 μm to 2 μm shows that the carbon nanotube composite coatings with such conical micro-structure have enhanced light absorptivity. It is also shown that the conical micro-structure with smaller cone angles exhibited much higher light absorptivity. It is proposed that carbon nanotube composite film being irradiated by laser is a simple and efficient method to fabricate black coatings with high light absorptivity.

INTRODUCTION

Black coatings with high solar absorptivity are of paramount importance for numerous applications, such as high efficiency absorbers or emitters for energy conversion, radiometers and bolometers for infrared thermal detectors, and other photonic devices [1-6]. Due to the π band's optical transition, novel structures, nanoscale dimension with high aspect radios as well as sparse tube to tube spacing, vertically aligned carbon nanotube arrays have achieved extremely high absorption [7-10]. It had been present that vertically aligned carbon nanotube (VACNT) arrays had lowest reflectance of about 0.045% and behaved most similarly to a black body that is an ideal object absorbing all light that falls on it [7, 8]. So it is proposed that carbon nanotubes may have great potential applications in those devices. Unfortunately, VACNT arrays can’t be synthesized on any substrates, which greatly limits the applications of VACNT arrays. On the other hands, tangled carbon

Liu Yuming\textsuperscript{a,*}, Yang Xiaoning, Li Man and Zhang Kai
Beijing Institute of Spacecraft Environment Engineering, Beijing 100084, P. R. China
\textsuperscript{a}lyming2005@126.com
\textsuperscript{*Corresponding author: lyming2005@126.com

724
nanotube films or carbon nanotube composite thin films which can be easily coated on any substrates exhibit higher reflectance and lower absorptivity than VACNT arrays [8, 11].

Obviously, the surface morphology can greatly affect the absorptivity of light-absorbing materials. The micrometer scale structure on the surface of the light-absorbing materials may have enhanced ability to absorb light [12, 13]. So it is a possible method to enhance the light absorbing ability of the carbon nanotube composite thin films by fabricating regular and uniform micrometer scale structure on them. In this work, enhancement of light absorbing properties of conical micro-structure on the surface of cyanoacrylate–carbon nanotube composite coatings was studied.

**EXPERIMENTAL**

Fabrication conical micro-structure on the surface of carbon nanotube composite coatings had been reported before [14]. Briefly, multiwalled carbon nanotube mats were mixed with cyanoacrylate adhesive by a weight ratio of 1:5. Then the slurry of carbon nanotube composites was coated on a substrate. The obtained cyanoacrylate-carbon nanotube composite coatings were irradiated in air with a normally incident laser beam. Then the near-normal spectral reflectance of the composite coatings before and after laser irradiation was measured in the 0.25-2.0μm wavelength with a SHIMADZU UV-3600 spectrophotometer.

**RESULT AND DISCUSSION**

Fig.1 shows the SEM images of the surface morphologies of the as-prepared sample and the irradiated sample. The morphologies of the cyanoacrylate-carbon nanotube composite coatings are much flat without any regular microstructures. It is clearly noted that aligned conical micro-structures have been fabricated on the surface of the coatings after laser irradiation.

![Figure 1. SEM images of the cyanoacrylate–carbon nanotube composite films before and after laser irradiation.](image-url)
It had been presented that the morphologies of the micro-cones obtained greatly depend on the laser irradiation fluence [14]. The surface of the composite films could not be etched by laser irradiation when the laser irradiation fluence is below 0.8 J/cm$^2$. When the laser irradiation fluence is at a level of 1.5 J/cm$^2$, many microcones could be produced with an average cone angle of about 45° as shown in Fig.2 (a). If the laser irradiation fluence is increased to 2 J/cm$^2$, the microcones obtained are much sharper with an average cone angle of about 25° as shown in Fig.2 (b). When the laser irradiation fluence is above 3 J/cm$^2$, the composite films will be etched away gradually without any conical microstructures formed. Here two samples with an average cone angle of about 45° and 25° respectively are used to study the enhancement of light absorptivity.

**Figure 2.** The microcones obtained on the surface of cyanoacrylate-carbon nanotube composites by laser irradiation. (a) at 1.5 J/cm$^2$, (b) at 2 J/cm$^2$.

The measured reflectance spectra of the three samples are shown in Fig.3 in the wavelength region form 250 nm to 2000 nm. Sample 1 is the one as prepared. Sample 2 and sample 3 are the samples irradiated by laser pulses at 1.5 J/cm$^2$ and 2.0 J/cm$^2$ respectively. The cone angles of sample 2 and sample 3 are 45° and 25° respectively. Because the reflectance spectrum of a BaSO$_4$ white coating is used as base line in SHIMADZU UV-3600 spectrophotometer, it is difficult to achieve high accuracy in the reflectance measurement. The reflectance spectra measured here are relative values.
The reflectance of sample 1 is very stable from near infrared to middle infrared. But the reflectance increases slightly from visible to ultraviolet. From the total reflectance measurement, those at 250nm, 500nm, 750nm, 1000nm, and 1500nm are obtained as about 5.6%, 3.6%, 3.2%, 2.4%, and 2.6% respectively, which means the corresponding absorptivity is 94.4%, 96.4%, 96.8%, 97.6%, and 97.4% respectively. It is seen that the reflectance of the sample decreases clearly in the whole measured wavelength range after laser irradiation. It’s also presented that sample 3 exhibits the lowest reflectance and the reflectance at 250nm, 500nm, 750nm, 1000nm, and 1500nm are about 1.0%, 1.0%, 1.1%, 0.9%, and 1.2% respectively. It is obvious that the variations of the reflectance among the three samples are related to surface roughness of them. The surface is much flat on sample 1, while microcones are formed on the sample 2 and sample 3. The incident light will be reflected and absorbed more than one time on the conical structure, so enhanced light absorptivity will be obtained. Moreover, the reflectance of sample 3 is lower than sample 2 because the angle of the microcones on sample 3 is much smaller.

There are two main reasons for the enhanced light absorptivity of the composite coatings after laser irradiation.

Firstly, carbon nanotubes are exposed after laser irradiation. The surface of the as-prepared sample is covered with a layer of cyanoacrylate as shown in Fig.4 (a). Carbon nanotubes immerge in the composites and can’t be observed. After laser irradiation, carbon nanotubes can be clearly observed on the tips of the cones as shown in Fig.4 (b). Carbon nanotubes are good absorber because of the $\pi$-band’s optical transitions [8], while cyanoacrylate has higher reflectance. When a layer of cyanoacrylate on the surface of the composite is etched away and carbon nanotubes are exposed, the optical properties of the coatings have been changed. So higher absorptivity can be obtained after laser irradiation.

Figure 3. Reflectance spectra of cyanoacrylate-carbon nanotube composite films before and after laser irradiation.
Secondly, we attribute this enhanced light absorptivity to multi-reflection of the incident light on the conical micro-structure. Obviously, incident light would all be reflected more than one time if the surface of a light absorber has conical structure with cone angle less than 90°. The times of being reflected depend on the cone angle of the conical structure. The smaller of the cone angle, the much more times of reflection. If the reflectance of a flat surface is \( r \) and the total absorption of the surface with conical micro-structure is \( A \), then we have \( A=1-r^n \) approximatively, where “n” is the times of reflection. So although the optical properties of the surface of sample 2 and sample 3 are the same, sample 3 with smaller cone angle have higher light absorptivity than sample 2.

A possible mechanism for the fabrication of microcones by excimer laser ablation on cyanoacrylate-carbon nanotube composites had been proposed [14]. It seems that the tips of the micro-cones, which may be resistant to laser irradiation at some fluence, play an important role for the formation of conical structures. To verify the mechanism, a new sample was first irradiated to form some microcones by 500 laser pulses with irradiation fluence of 1.5J/cm\(^2\). Then a laser pulse with much higher irradiation fluence of 3.0J/cm\(^2\) irradiated the sample to etch the tips away. Finally, the sample was irradiated by laser pulses with irradiation fluence of 1.5J/cm\(^2\) again.

Fig. 5 shows the surface morphologies of the samples at different stages. It is shown that some small microcones have been formed after laser irradiation with fluence of 1.5 J/cm\(^2\) (Fig.5 (a)). If the sample were irradiated continuously with the same irradiation condition of laser irradiation fluence of 1.5 J/cm\(^2\), the large area microcones would be obtained just as shown in Fig.2 (a). But a laser pulse with fluence of 3.0 J/cm\(^2\) was used to irradiate the sample, then the sample were irradiated continuously with the same irradiation condition of laser irradiation fluence of 1.5

![Figure 4. Enlarged SEM images of the cyanoacrylate–carbon nanotube composite films before and after laser irradiation. (a) Before irradiation. (b) After irradiation.](image)
J/cm\(^2\). The different phenomenon is presented that the microcones which have been obtained are etched down from the tops gradually by further laser irradiation (Fig. 5 (b) (c)), while the bottom of the microcones still maintains the conical shape.

![Image](image_url)

**Figure 5.** The three stages of surface morphology in cyanoacrylate-carbon nanotube composite films by excimer laser irradiation. (a) After 500 laser pulses at 1.5 J/cm\(^2\). (b) After 1 more laser pulse at 3.0 J/cm\(^2\) and 500 more laser pulses at 1.5 J/cm\(^2\). (c) After 500 more laser pulses at 1.5 J/cm\(^2\). (d) Schematics of the mechanism for the three stages.

When the laser irradiation fluence is increased to 3.0J/cm\(^2\), the energy density is high enough to etch the tips of the microcones away. Although the laser irradiation fluence is decreased to 1.5J/cm\(^2\) again, the laser energy density is enough to etch down the flat tops of the microcones. As a result, the microcones will be etched down from the tops gradually. On the other hand, the slopes of the microcones have nearly no change by only one higher energy laser pulse irradiation, so the conical shape of the slopes can be maintained. The mechanism for this phenomenon is shown schematically in Fig 5(d).

**SUMMARY**

We have shown that the self-organized microcones can be formed on carbon nanotube composite films by a simple laser irradiation method in a proper irradiation fluence range. The angles of the microcones formed are related to the laser irradiation fluence. It has been confirmed that the mechanism of the formation of the microcones is due to the singular region in the composites. Such conical microstructure has enhanced light absorption properties because the incident light can be reflected and absorbed more than one time on such structures. The absorptivity can significantly increase after laser irradiation. The absorptivity of as-prepared sample is from 2.4% to 5.6% in the measured wavelength range, while the absorptivity of laser-treated sample is from 0.9% to 1.4%. The absorptivity has been increased by about 2 percent. It is proposed that laser irradiation is a simple and efficient method to fabricate conical microstructures on carbon nanotube composite and enhance their light absorption.
absorption properties. It may have potential application in developing super black coating materials for many applications such as pyroelectric detectors.

REFERENCES

[1] C. Nunes, V. Teixeira, M. Collares-Pereira, A. Monteiro, E. Roman, J. Martin-Gago, Deposition of PVD solar absorber coatings for high-efficiency thermal collectors. Vacuum 67 (2002) 623-627.
[2] A. R. Shashikala, A. K. Sharma, D. R. Bhandari, Solar selective black nickel-cobalt coatings on aluminum alloys, Sol. Energy Mater. Sol. Cells 91(7) (2007) 629-635.
[3] E. Theocharous, R. Deshpande, A. C. Dillon, J. Lehman, Evaluation of a pyroelectric detector with a carbon multiwalled nanotube black coating in the infrared, Appl. Opt. 45 (2006) 1093-1097.
[4] I. Mellouki, N. Bennaji, N. Yacoubi, IR characterization of graphite black-coating for cryogenic detectors, Infrared Phys. Tech. 50 (1) (2007) 58-62.
[5] T. Saito, K. Hayashi, H. Ishihara, I. Saito, Characterization of temporal response, spectral responsivity and its spatial uniformity in photoconductive diamond detectors, Diamond Relat. Mater. 14 (2005) 1984-1987.
[6] J. H. Lehman, C. Engrtrakul, T. Gennett, A. C. Dillon, Single-wall carbon nanotube coating on a pyroelectric detector, Appl. Opt. 44 (2005) 483-488.
[7] Z. P. Yang, L. Ci, J. A. Bur, S. Y. Lin, P. M. Ajayan, Experimental observation of an extremely dark material made by a low density nanotube array, Nano Lett. 8 (2008) 446-451.
[8] K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura, K. Hata, A black body absorber from vertically aligned single-walled carbon nanotubes, PNAS 106 (2009) 6044-6047.
[9] X. J. Wang, J. D. Flicker, B. J. Lee, W. J. Ready, Z. M. Zhang, Visible and near-infrared radiative properties of vertically aligned multi-walled carbon nanotubes, Nanotechnology 20 (2009) 215704.
[10] R. E. Camacho, A. R. Morgan, M. C. Flores, T. A. McLeod, V. S. Kumsomboone, B. J. Mordecai, R. Bhattacharjea, W. Tong, B. K. Wagner, J. D. Flicker, S. P. Turano, W. J. Ready, Carbon nanotube arrays for photovoltaic applications, JOM 59 (2007) 39-42.
[11] K. T. Roro, N. Tile, B. Mwikungu, B. Yalisi, A. Forbes, Solar absorption and thermal emission properties of multiwall carbon nanotube/nickel oxide nanocomposite thin films synthesized by sol-gel process, Mater. Sci. Eng. B 177 (2012) 581-587.
[12] E. Rephaeli, S. Fan, Absorber and emitter for solar thermo-photovoltaic systems to achieve efficiency exceeding the Shockley-Queisser limit, Opt. Express 17 (2009) 15145-15149.
[13] S. Kajita, T. Saeke, N. Yoshida, N. Ohno, A. Iwamae, Nanostructured black metal: Novel fabrication method by use of self-growing helium bubbles, Appl. Phys. Express 3 (2010) 085204.
[14] Y. M. Liu, L. L. Liu, S. S. Fan, Fabrication of self-organized conical microstructures by excimer laser irradiation of cyanoacrylate-carbon nanotube composites, Appl. Phys. Lett. 856 (2005) 063105.