

Carbon Nanotube Spectrally Selective Solar Absorbers

Zhonghua Chen¹, Quang Hong Nguyen¹ and Tobias Boström²

¹ Norut Northern Research Institute Narvik AS, Narvik, Norway

² UiT, The Arctic University of Norway, Department of Physics and Technology, Tromsø, Norway

Abstract

The use of multi-walled carbon nanotubes (MWCNTs) as spectrally selective solar thermal absorbers (SSA) in solar thermal collectors is presented in this paper. CNT layers were coated by electrophoretic deposition (EPD) on aluminum substrates. Stable aqueous CNT suspensions consisted of multi-walled CNTs, DI water and surfactant was used for EPD. The deposited samples were heat treated in a tube oven before any analysis. Various thicknesses and compositions of homogenous CNT coatings were prepared by tuning the electrophoretic parameters, such as voltage, inter-electrode spacing and deposition time. EPD proved to be a simple, feasible and environment-friendly process of fabricating SSA and has low chemical consumption. In order to achieve homogenous and good quality CNT films an EPD voltage of at least 15V has to be used. The effect of thickness and heat treatment of CNT coatings on the solar absorptance and thermal emittance was investigated. With thicker CNT coating, the absorption of SSA increased in both visible and IR spectral range. The results have indicated CNTs as a promising material for SSA. Different peak temperatures and the dwell time at the peak temperature during the heat treatment were applied to understand the effect. Higher heat treatment peak temperatures resulted in a lower thermal emittance without decreasing the solar absorptance; hence the spectral selectivity of CNT absorbers was improved. The same effect has been seen for longer dwell time at the heat treatment peak temperature.

Key-words: carbon nanotubes, solar absorber, spectral selectivity, electrophoretic deposition, thickness, reflectance, solar absorptance, thermal emittance.

1. Introduction

Spectrally selective solar thermal absorbers (SSA) are an essential element of solar thermal collectors and usually consist of two different layers, thus called tandem absorbers (Agnihotri and Gupta, 1981). Each of the two layers has unique optical properties. The top layer usually functions as a selective solar irradiation absorber and should be transparent to infrared irradiation. The substrate under the top layer reflects infrared light, i.e. giving the absorber low thermal emittance. Highly reflective metals such as aluminum and copper are commonly used. Together they give a good spectral selectivity over the solar and infrared spectrum.

Metal-dielectric composites, also referred to as cermet films, are well known as solar absorbing layers. However, such coatings are difficult to fabricate; they are normally produced using various vacuum deposition technologies such as sputtering or physical vapor deposition (PVD) which both are inherently complicated and expensive methods. However, PVD as a coating process has many advantages, such as good abrasion resistance, uniform and accurate control of thickness but the technology requires vacuum and often high temperatures. The absorbing layer can also be produced using painting and spin-coating of liquid solutions. Painting is an effective and inexpensive way, but has a poor control on the coating thickness which often results in a high thermal emittance and the coatings usually have inferior adhesion to the substrates. Spin-coating has been widely applied in the fabrication of thin films with nanoscale thicknesses using sol-gel precursors. High performance spectrally selective solar absorbers have been produced using this method (Boström et al., 2007). In our research, electrophoretic deposition (EPD) is used for the formation of CNT coatings. EPD is a facile process for fabrication of films and coatings from aqueous or organic suspensions

on substrates and bulk bodies with even complicated surfaces. Electrophoretically deposited coatings exhibits good microstructure homogeneity and the thickness of coating can be easily controlled by tuning the EPD parameters, such as voltage, inter-electrode spacing, deposition time (Boccaccini and Zhitomirsky, 2002). EPD has been successfully employed to deposit CNTs on various substrates by many researches (Boccaccini et al. 2006; Du et al., 2002; Fraczek-Szezypta et al., 2013; Nakayama et al., 2001; Thomas and Boccaccini, 2005).

Carbon nanotubes (CNTs), discovered by Iijima (1991), have been extensively studied due to their unique thermal, electronic and mechanical properties. They have also a very high absorbance at light wavelengths from far ultraviolet to near infrared (Wu et al., 2003). Cao et al. (2002) had prepared a tandem structure by synthesizing aligned CNTs on Au films to investigate the solar thermal absorption. Their conclusion was that the tandem structure has no spectral selectivity in solar absorption though a high absorptance of 95% was gained in both the visible and infrared regions. Schultz (2006) patented a solar absorptive coating system consisting of CNTs. The highest solar absorptance achieved was 0.71 which is too low compared to commercial products. In this paper, we report the performance of CNT absorbers manufactured by the EPD method.

2. Method

A CNT slurry from n-Tec AS (Oslo, Norway) was used as CNT source for electrophoretic deposition, consisting of DI water, Multi-walled carbon nanotubes (MWCNT) and a surfactant. According to the supplier, MWCNT were synthesized by arc discharge and then purified. The diameter of MWCNTs is 10-50nm and the typical length is 2-5 μ m. To make kinetically stable aqueous suspensions of CNTs, the MWCNTs were functionalized and a surfactant was added into the solutions to stabilize MWCNTs. Then a sonication process was applied to disperse the MWCNTs. The CNT slurry is stable over months. The CNT slurry was used and ultrasonicated every time before EPD experiments since CNTs tend to form aggregates over time.

A schematic diagram of EPD is shown in Fig.1a. Two electrodes made of aluminum plates, of which the anode is also used as the CNT absorber substrate, are connected to a DC power supply. Aluminum was used due to its ease of availability, low density and most importantly its high reflectance in the infrared wavelength region. The aluminum plate was from Metallvaruhuset AB in Sweden and was cut in squares of 3x3cm² and cleaned before usage. During EPD, the two aluminum substrates were immersed in CNT slurry contained by a glass beaker. The surfactant type determines on which of the electrodes the CNTs are deposited. Charged CNTs by anionic or cationic surfactant move to the opposite electrode i.e. substrate. In our experiments, CNTs were deposited on anode since the used surfactant in CNT slurry is anionic.

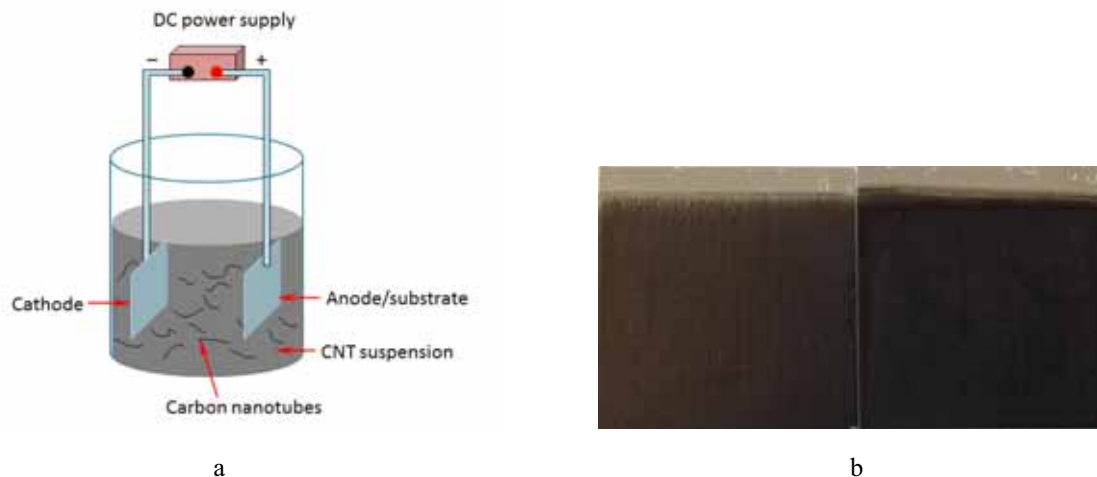


Fig. 1: Electrophoretic deposition of carbon nanotubes. a) Schematic diagram of EPD of CNTs; b) Sample of CNT absorber.

After deposition, the samples were taken out of CNT slurry gently to avoid the removal of CNTs. Then the samples were dried in room conditions for at least 16 hours before heat treated in a tube oven.

The profile of heat treatment consisted of two phases – warming-up and peak temperature. The heating rate of warming-up phase was set to 50°C per minute. The peak temperature was set to different points depending on the intention of experiment. When the peak temperature was reached, the samples were in one experiment treated at the peak temperature for a period i.e. dwell time. After the dwell time, the power of tube oven was shut down and it allowed the temperature decreased slowly. When the temperature declined to 300°C, the samples were taken out of the oven and cooled to room temperature in the air. Thereafter the samples were ready for any measurements and analysis.

In the experiments of EPD, the voltage was initially set to 5V while keeping an inter-electrode spacing of 1 cm, i.e. the electric field equals to 5V/cm. With this voltage, there was very little CNTs deposit and importantly it was loosely attached to the aluminum substrate and was almost completely removed while the sample was taken out of the suspension. An increase of deposition time did not improve on the quality of the CNT coating. The EPD voltage was increased step by step to get uniform coating and a voltage threshold was found to be 15V for a robust and uniform CNT coating. This phenomenon about a voltage threshold for EPD of CNT was also noticed by Thomas et al. (2006). But a voltage threshold of 30V was discovered in their suspension system. The difference of voltage threshold must be due to the different suspension systems which relate to the type and concentration of CNT and surfactant. This voltage threshold can be explained by a weaker adherence between CNTs and substrate for a lower voltage. Above the voltage threshold, the CNTs deposit has sufficient adhesion to the substrate and the coating quality is improved.

To understand more about the phenomenon, a certain electric field of 10V/cm was kept with the voltage being 10V, 20V, 30V and the inter-electrode spacing being 1cm, 2cm and 3cm, respectively. It is found that the deposition yield increased with higher voltage. Uniform deposition was obtained for the conditions of 20V and 30V. This indicates that the voltage is more important than the electric field regarding the threshold.

For a too high voltage during EPD, CNTs tend to form aggregates. In order to get the best quality of CNT coatings, a voltage of 25V and an inter-electrode spacing of 2cm were ultimately used in the EPD experiments. The deposition time ranges from only 4 to 16 seconds to get a thin CNT coating on an aluminum substrate working as an absorbing layer. The thickness of the CNT coating and corresponding deposition times are presented in the discussion section.

3. Characterization

3.1. Characterization tools

Thickness of the CNT coatings was examined by Veeco NT9080 Profilometer which uses high precision white light interferometry in order to analyze height differences. Surface morphology and atomic composition of the samples were investigated using a ZEISS Merlin VP Scanning Electron Microscope equipped with an EDS detector from Oxford Instruments. The adhesion between CNT coating and Al substrate was evaluated by tape test. To characterize absorption properties of SSA samples, a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere of diameter 150mm, circular beam entrance and sample port of 25mm, was used in the wavelength interval 0.3-2.5 μ m. Emittance of the samples in the infrared wavelength range 2.5-20 μ m was measured with a Bruker Tensor27 FT-IR spectrophotometer.

3.2. Optical characterization

A SSA is usually evaluated by two parameters – the solar absorptance and the thermal emittance under a normal angle of incident radiation. Normal solar absorptance, α , is theoretically defined as a weighted fraction of the absorbed radiation to the incoming solar radiation on a surface, see Equation (1). The spectral solar irradiance, I_{sol} , is defined according to ISO standard 9845-1 (1992) for air mass of 1.5. λ is the wavelength of incident radiation in the unit of μ m and $\rho(\lambda)$ is the reflectance at a certain wavelength.

$$\alpha = \frac{\int_{0.3}^{2.5} I_{sol}(\lambda)(1 - \rho(\lambda))d(\lambda)}{\int_{0.3}^{2.5} I_{sol}(\lambda)d(\lambda)} \quad (\text{eq. 1})$$

Normal thermal emittance, ε , is the ratio of emitted radiation of a surface to that of Plank's blackbody, I_p , at 100°C and can be calculated following Equation (2):

$$\varepsilon = \frac{\int_{2.5}^{20} I_p(\lambda)(1 - \rho(\lambda))d(\lambda)}{\int_{2.5}^{20} I_p(\lambda)d(\lambda)} \quad (\text{eq. 2})$$

There are several ways to evaluate the spectral selectivity. One of the most frequent used methods is to calculate the ratio of solar absorptance and thermal emittance (α/ε). However, we judge this method as very inequitable. For example, a solar absorber with a solar absorptance of 0.60 and a thermal emittance of 0.03 achieves a ratio of 20 but doesn't have higher photothermal conversion efficiency than an absorber with a solar absorptance of 0.90 and a thermal emittance of 0.1 which achieves a ratio of only 9. The opposite is actually true since the solar absorptance is twice as important as the thermal emittance. In order to rate the selectivity and hence the performance of a solar absorber we are in this paper using the formula $\alpha-0.5\varepsilon$ which reflects the weight factor of thermal emittance in a more reasonable matter. The formula was first recommended by Carlsson (2004) in a report from IEA solar heating and cooling program Task 27.

4. Results and discussion

4.1. Surface morphology

Fig.2 shows SEM images from two samples prepared with an EPD voltage of 25V and an inter-electrode spacing of 2cm. Sample 1(Fig.2a) was deposited for 4 seconds and the CNT coating has a thickness of 0.95 μm . Sample 2 (Fig.2b) was deposited for 10s with a CNT layer of 1.70 μm . Both images indicate that in the coatings there are a lot of CNTs which are parallel to the substrates. The nanoparticles seen around the CNTs displayed in Fig.2b are expected to be graphite nanoparticles and graphitic impurities from the original MWCNT product. However, that hypothesis needs to be verified with for example Raman spectroscopy. The EDS result of Sample 2 is shown in Fig.3. Mostly 4 elements – C, O, Al and S were detected by EDS. Since the aluminum substrate was used as-produced, most of Al and O are from the substrate and its 10nm native protective layer of alumina. The sulfur content found in the EDS analysis is likely to stem from the anionic groups of surfactant which contain sulfur.

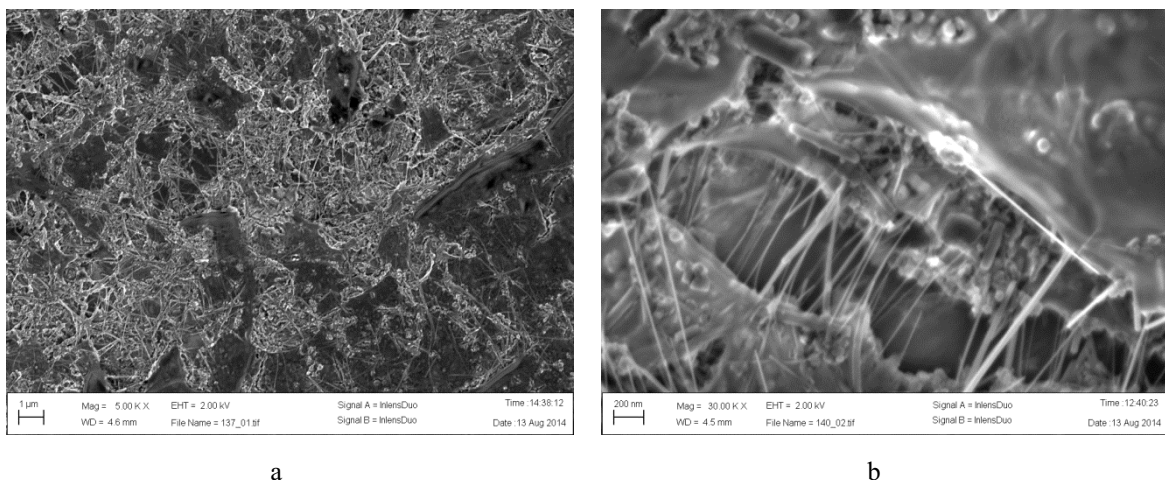


Fig. 2: SEM images of CNT absorbers, a) Sample 1 under a magnification of 5K; b) Sample 2 under a magnification of 30K.

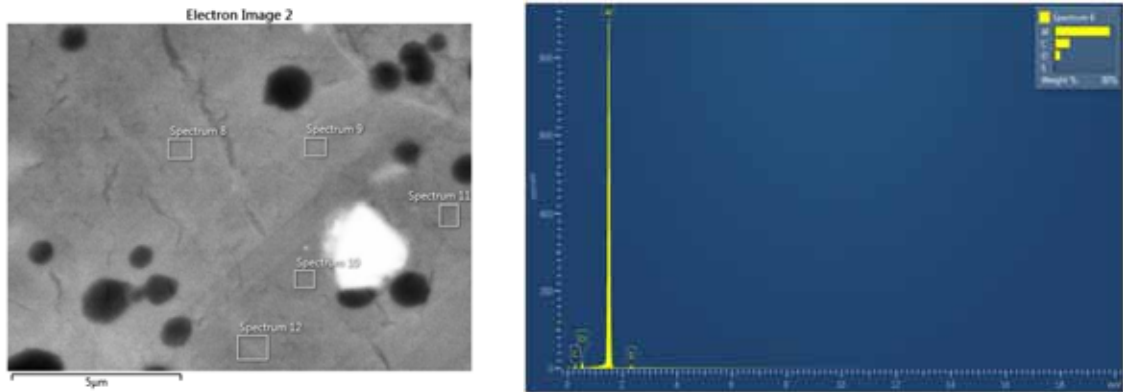


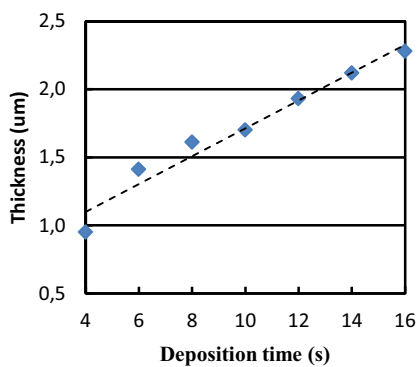
Fig. 3: EDS result of Sample 2.

4.2. Effect of CNT coating thickness

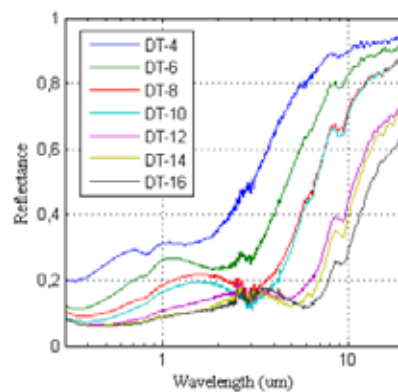
To investigate the effect of CNT coating thickness, a series of samples were made with the deposition time varied from 4 to 16 seconds (shown in Tab.1). The EPD voltage was 25V and the inter-electrode spacing was 2cm. All the samples were heat treated with a peak temperature of 550°C and then directly cooled to room temperature. The calculated solar absorptance, thermal emittance and selectivity are presented in Tab.1. With longer deposition time, the thickness of CNT coatings increases almost linearly, the minor deviation of nonlinearity is probably due to measurement inaccuracy and slightly different deposition for each sample. The transition from low to high reflectance shifted to longer wavelength with increasing thickness of CNT coatings. The best selectivity achieved at the CNT coating thickness of 1.70 μm was 0.72 with a solar absorptance of 0.87 and a thermal emittance of 0.30.

Tab. 1: The effect of deposition time on solar absorptance and thermal emittance of SSA

Samples	Deposition time (s)	Coating thickness (μm)	Absorptance (α)	Emittance (ϵ)	Selectivity
DT-4	4	0.95	0.71	0.11	0.66
DT-6	6	1.41	0.79	0.19	0.70
DT-8	8	1.61	0.85	0.29	0.71
DT-10	10	1.70	0.87	0.30	0.72
DT-12	12	1.93	0.91	0.50	0.66
DT-14	14	2.12	0.92	0.54	0.65
DT-16	16	2.28	0.92	0.61	0.62



a



b

Fig. 4: Thickness (a) and reflectance (b) of CNT absorbers deposited with various time from 4 to 16 seconds.

4.3. Effect of peak temperature in heat treatment

The effect of the peak temperature during the heat treatment on the performance of CNT absorbers were studied by two groups of samples, thin CNT coatings deposited for 5s and thick CNT coating deposited for 9s. The voltage of EPD was 25V and the inter-electrode spacing was 2cm. For the group of absorbers with thin CNT coatings, they were heat treated at different peak temperatures, 400, 500 and 600°C while the samples with thick CNT coatings were treated at peak temperatures of 450, 550 and 650°C separately. The result from both groups indicated an improved spectral selectivity with a higher peak temperature. It is worth noting that higher peak temperature prolongs the duration for absorbers staying in the oven. One thing needs to be noticed is that temperature over 650°C is not desired since pure aluminum has a melting point of 660°C.

Tab. 2: The effect of peak temperature of heat treatment on selectivity of SSA with thin CNT coatings

Samples	Deposition time (s)	Peak temperature (°C)	Absorptance (α)	Emittance (ϵ)	Selectivity
Thin-400	5	400	0.80	0.22	0.69
Thin -500	5	500	0.81	0.19	0.71
Thin -600	5	600	0.79	0.14	0.72

Tab. 3: The effect of peak temperature of heat treatment on selectivity of SSA with thick CNT coatings

Samples	Deposition time (s)	Peak temperature (°C)	Absorptance (α)	Emittance (ϵ)	Selectivity
Thick-450	9	450	0.88	0.51	0.63
Thick-550	9	550	0.87	0.37	0.69
Thick-650	9	650	0.87	0.29	0.73

4.4. Effect of dwell time in heat treatment

18 samples were prepared with same EPD parameters, a voltage of 25V, an inter-electrode spacing of 2cm, and a deposition time of 10s. They were divided to 6 groups, 3 for each of them. The peak temperature during the heat treatment was 500°C for all 6 groups, but the dwell time was set to 0, 5, 10, 15, 20 and 30 minutes for each group respectively. Tab.4 gives the average numbers of absorptance, emittance and selectivity for each group. When the dwell time increased from 0 to 5 minutes, the emittance had a clear drop while the absorptance was kept almost unchanged, which resulted in a gain in selectivity. Any additional increase in dwell time only slightly lowers the emittance further. It is believed that the decrease in emittance with dwell time is caused by evaporation or outgassing of the infrared absorptive surfactant material in the CNT films. It is likely that the largest evaporation occurs initially and then exponentially decreases which could explain the trend seen in Tab.4.

Tab. 4: The composition of CNT coatings with different dwell time

Samples	Dwell time (min)	Absorptance (α)	Emittance (ϵ)	Selectivity
D0	0	0.89	0.39	0.70
D5	5	0.88	0.32	0.72
D10	10	0.87	0.32	0.71
D15	15	0.88	0.31	0.73
D20	20	0.88	0.29	0.74
D30	30	0.88	0.28	0.74

5. Conclusion

Carbon nanotube spectrally selective absorbers were successfully prepared by the method of electrophoretic deposition. The CNT coatings are homogeneous according to SEM images and have a reasonable adhesion to the aluminum substrates. CNT absorbers exhibit fairly good selectivity over the solar and infrared spectrum which indicates that this material is a potential candidate for use as spectrally selective absorbers in solar thermal collectors. A voltage threshold for EPD was found to be 15V for the used CNT suspension system. The thickness of CNT coatings is linearly increasing with the deposition time. With thicker CNT coating, the transition from low to high reflectance of solar absorbers shifts to longer wavelength which benefits the solar absorptance but increases the thermal emittance in the meantime. Both higher peak temperature and longer dwell time at the peak temperature during the heat treatment improved the spectral selectivity of the CNT absorbers. More experiments need to be carried out in order to find the optimum conditions of heat treatment. The best performance achieved was a solar absorptance of 0.88 and a thermal emittance of 0.28 which yielded a selectivity of 0.74. However, the selectivity of the CNT absorbers is still not good enough compared to commercial solar absorber products. Further improvement could be done by adding an anti-reflection layer on the top of CNT coating and/or by modifying the CNT layer composition.

Acknowledgements

This work was supported by Nano2021 program of the research council of Norway and the company ASV Solar AS.

References

- Agnihotri, O.P., Gupta, B.K., 1981. *Solar Selective Surfaces*. John Wiley & Sons, New York.
- Boccaccini, A.R., Zhitomirsky, I., 2002. Application of electrophoretic and electrolytic deposition techniques in ceramics processing. *Current Opin Solid State Mater Sci.* 6, 251–60.
- Boccaccini, A. R., Cho, J., Roether, J.A., Thomas, B.J.C., Minay, E.J., Shaffer, M.S.P., 2006. Electrophoretic deposition of carbon nanotubes. *Carbon.* 44, 3149-3160.
- Boström, T., Westin, G., Wäckelgård, E., 2007. Optimization of a solution-chemically derived solar absorbing spectrally selective surface. *Solar Energy Materials and Solar Cells.* 91, 38-43.
- Cao, A., Zhang, X., Xu, C., W, B., Wu, D., 2002. Tandem structure of aligned carbon nanotubes on Au and its solar thermal absorption. *Solar Energy Materials and Solar Cells.* 70, 481-486.
- Carlsson, B., 2004. Recommended qualification test procedure for solar absorber surface durability. IEA SHC Task 27 draft report.
- Du, C., Heldbrant, D., Pan, N., 2002. Preparation and preliminary property study of carbon nanotubes films by electrophoretic deposition. *Materials Letters.* 57, 434-438.
- Fraczek-Szczypta, A., Dlugon, E., Weselucha-Birczynska, A., Nocun, M., Blazewicz, M., 2013. Multi walled carbon nanotubes deposited on metal substrate using EPD technique: A spectroscopic study. *Journal of Molecular Structure.* 1040, 238-245.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature.* 354, 56–58.
- Nakayama, Y., Akita S., 2001. Field-emission device with carbon nanotubes for a flat panel display. *Synthetic Metals.* 117, 207-210.
- Schultz, F.S., Solar absorptive coating system. US Patent. Pub. No. 2009/0314284.
- Thomas, B.J.C., Boccaccini, A.R., 2005. Multi- Walled Carbon Nanotube Coatings Using Electrophoretic Deposition (EPD). *J. Am. Ceram. Soc.* 88, 980-982.
- Thomas, B.J.C., Shaffer, M.S.P., Freeman, S., Koopman, M., Chawla, K.K., Boccaccini, A.R., 2006.

Electrophoretic deposition of carbon nanotubes on metallic surfaces. *Key Engineering Materials*. 314, 141-146.

Wu, X., Pan, L., Li, H., Fan, X., Ng, T.Y., Xu, D., 2003. Optical properties of aligned carbon nanotubes. *Phys. Rev. B*. 68, 193401.