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MICROWAVE ENERGY-ASSISTED FABRICATION OF HIERARCHICALLY STRUCTURED CARBON NANOTUBE/CARBON FIBER COMPOSITES

Selçuk POYRAZ *

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Abstract: Through a facile, simple, yet efficient, affordable and ultrafast (30 s) microwave (MW) energy heating process, hierarchical composites made up of carbon fibers (CFs) decorated with multi-walled carbon nanotube (MWCNT) forest were produced at ambient conditions in one-step. Morphological features of the as-produced composites were characterized in details by using scanning and transmission electron microscopy (SEM, TEM) and the elemental analysis (EDX) techniques. Both the composite material characterization results and the versatile and easily controllable nature of the above mentioned process strongly support its promising success for the fabrication of such hierarchical composites that could be effectively used for the next generation advanced engineering applications.

Keywords: Microwave energy, Carbon nanotube, Carbon fiber, Hierarchical composite

Mikrodalga Enerjisi Yardımıyla Hiyerarşik Yapılı Karbon Nanotüp/Karbon Lifi Kompozitlerinin Üretilmesi

Öz: Zahmetsiz, sade ve basit buna rağmen oldukça verimli, hesaplı ve kısa süreli (30 s) mikrodalga enerjisi tabanlı bir ısıtma işlemi kullanılarak; yüzeyini çok duvarlı karbon nanotüplerin ormanımsı bir tabaka halinde kapladığı karbon liflerinden oluşan hiyerarşik yapıdaki kompozitler ortam koşullarında tek adımda üretilmiştir. Üretilen bu kompozit yapıların morfolojik özellikleri, taramalı ve geçirimli elektron mikroskopları kullanılarak ve elementel analiz yardımıyla detaylıca test edilmiştir. Hem elde edilen kompozit malzeme özelliklerinin test sonuçları hem de bahsedilen bu işlemin çok yönlü ve kolaylıkla kontrol edilebilir sistematiği, yöntemin, yeni nesil ileri mühendislik uygulamalarında etkin olarak kullanılabilecek bu tip hiyerarşik yapıdaki kompozitlerin üretilmesindeki umut vaat eden başarısını kuvvetli bir biçimde desteklemektedir.

Anahtar Kelimeler: Mikrodalga enerjisi, Karbon nanotüp, Karbon lifi, Hiyerarşik yapılı kompozit

1. INTRODUCTION

Not only because of its excellent mechanical strength but also its thermal and electrical conductivity, light weight and high processability, CF and its products have been extensively utilized as a building material in various advanced engineering systems such as aerospace ships, communication satellites, planes, hybrid vehicles, wind turbine blades, sports equipment, prosthetic limbs and so on (Chand, 2000). As an expected result of its unique fibrous structure, CF usually serves as a reinforcing component to enhance the multi-scale properties of the above mentioned bulk composite materials made up of both thermoset and thermoplastic polymers, metals and concrete, as well Thostenson et al., (2001). A great deal of research effort has been devoted to enhance the reinforcing performance of CFs, in order to; (i) reduce or even eliminate

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* Department of Textile Engineering, Corlu Faculty of Engineering, Namik Kemal University, Corlu, Tekirdag 59860

Correspondence Author: Selçuk Poyraz (spoyraz@nku.edu.tr)

the problems that are often caused by phase separation and also shearing upon excessive and repeating stress, and (ii) to achieve strong, light-weight, durable and high performance composite materials that can be used for a wide variety of real-life engineering applications Delamar et al., (1997), Xu et al., (2006), Yuan et al., (2012).

In recent years, CNT growth on CF surface has been proposed as a promising solution in order to address the needs and tackle the challenges in the above mentioned matters, since a nanostructured, 3D CNT forest surrounding the CF surface can both provide sufficient number of anchoring points and can significantly increase the effective specific surface area to reach a better adhesion performance between CFs and the bulk material matrix Thostenson et al., (2002), Samsur et al., (2013), Yu et al., (2014). Moreover, with the addition of distinct mechanical, thermal, and electrical features of the CNTs into the structure, enhanced transverse and shear resistance can also be expected from the as-produced CNT/CF hierarchical composites, as a result of the intense interfacial interactions that exist between the as-grown CNT forest and CFs.

In general, the CNT forest is grown on the CFs' surface by following either a bottom-up method such as chemical vapor deposition (CVD) or a top-down method such as lithography Zhao et al., (2005), Chen et al., (2010). Although these methods can provide highly precise and uniform products, they usually suffer from their complex production process and from their need of harsh process conditions, i.e. high vacuum, high temperature, high pressure and hazardous chemicals' use. Additionally, these methods' overall fabrication processes are not easily scalable and are very time consuming, as well. Thus, the as-obtained sample amounts are usually limited and this restricts the common uses of such methods for the applications at industrial level. In order to eliminate these obstacles and to realize a practical application for the CNT/CF composites preparation, in this study, a well-established MW energy-assisted fabrication technique, which can rapidly grow a homogenous MWCNT forest decoration on CFs surface, is proposed Liu et al., (2011). The as-prepared CNT/CF composites from this method offer promising and wide range application potential for various advanced engineering and scientific fields including fiber reinforced composites' preparation for wind energy harvesting, super-capacitance, microelectronics, telecommunication, transportation, sports equipment and medical applications.

2. MATERIALS AND METHODS

2.1. Materials Used

Plain weave CF fabric, acetone (JT Baker), toluene (JT Baker) and ferrocene (AlfaAesar) were all used as purchased without further purification, unless otherwise specified.

2.2. Pre-treatment and Preparation of CF Mesh Samples

Prior to the MW energy-assisted rapid CNT forest growth process, several 1"×1" CF fabric samples were continuously heated in a conventional kitchen MW oven (Panasonic Inverter) at full power (1250 W) for 60 s, in order to; (i) remove the protective thin sizing layer, and (ii) to reveal as much reactive sites as possible on CFs' surface for the following process steps (Figure 1). Next, 0.2 M ferrocene solution was prepared by dissolving 0.11 moles of ferrocene in 550 mL of toluene, for the homogenous deposition of the carbon and catalyst source precursor chemical on the as-treated CF samples. After that, CF fabrics were individually soaked into this solution for 10 min under continuous gentle shaking. Eventually, all the samples were drip dried on a nylon string before the ultrafast MW heating process (Figure 2).

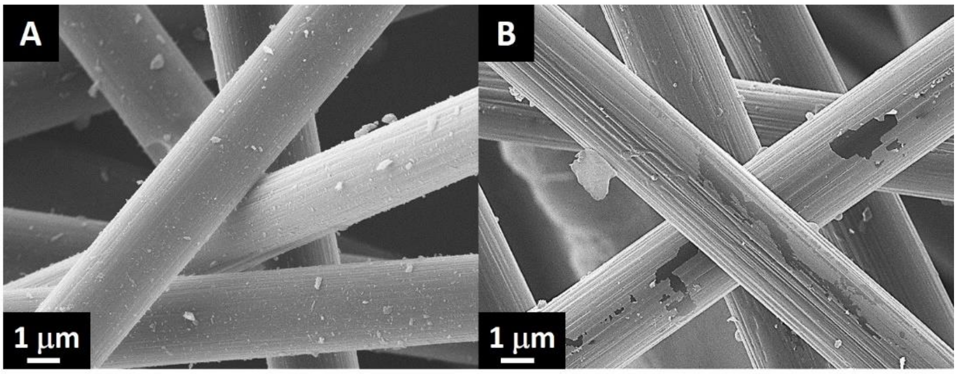

Figure 1:
Scanning electron microscopy (SEM) images of CFs; ***A.*** *before and* ***B.*** *after MW pre-treatment.*

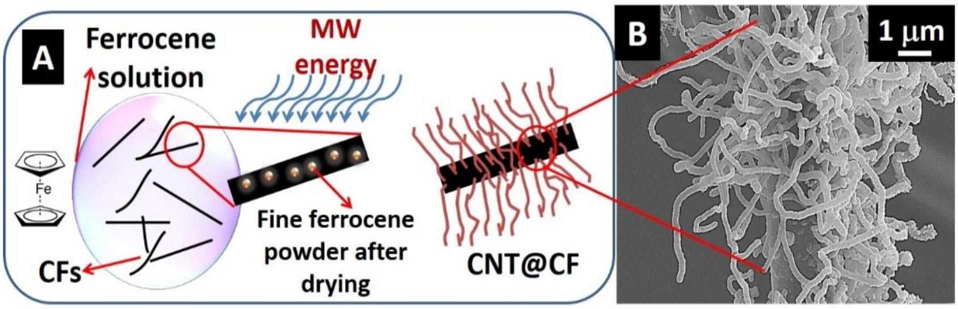

Figure 2:
A. *Schematic representation of the MW energy-assisted ultrafast CNT forest growth process on CFs,* ***B.*** *SEM image of a single CF covered by CNT forest on its surface.*

2.3. MW Energy-assisted Ultrafast CNT Forest Growth Process on CFs

The as-prepared CF fabric sample was tightened vertically between a pair of glass rods on a handmade PVC stand, and then it was placed on the glass MW tray. Here, the evenly deposited thin ferrocene layer was clearly observed on the CF fabric with an orange tint. The glass tray was then placed into the MW oven chamber. The CF fabric on the PVC stand was irradiated at the maximum power level, while intensive reactions were observed inside, as indicated by the sparking flames and dense chemical vapor emission. After getting heated by MWs for 30 s, the CF fabric sample with the as-grown CNT forest decoration on its surface was taken out and then gently rinsed with acetone to remove any impurities and unreacted chemicals (Figure 3).

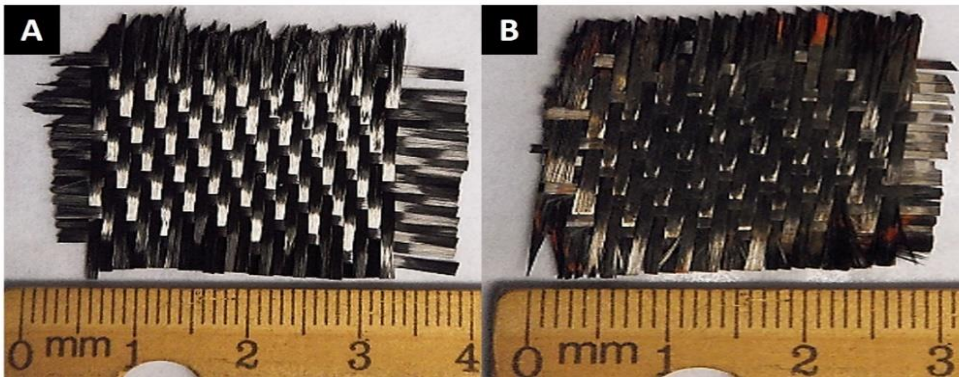

Figure 3:
Digital images of a CF fabric sample; ***A.*** *before and* ***B.*** *after the MW energy-assisted ultrafast CNT forest growth process.*

2.4. Characterization of the As-prepared Composite Material

Morphological and elemental analyses of the as-obtained composite materials were done by using a JEOL JSM-7000F scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detector. An EMS 550X auto sputter coating device was also utilized for surface Au sputter coating of composite samples, which were readily prepared on carbon tape mounted sample holders, prior to their analysis. The in-depth morphological property analysis of the as-prepared composites was performed on a JEOL 2100F transmission electron microscope (TEM), operated at 200 kV. Here, CF strands from the as-treated fabric sample were carefully removed and dispersed in ethyl alcohol by ultrasonication for 10 min. in order to separate the as-grown CNTs from the CFs. Next, droplets (~5μL) from the supernatant surface were collected with a pipette and then transferred onto a carbon coated copper Formvar grid and left to get dried at ambient conditions before TEM testing.

3. RESULTS AND DISCUSSION

After the MW heating process, a dense CNT forest layer was intensively grown on the CF fabric surface and covered almost the entire fiber surface with a radially aligned and entangled assembly look, which is clearly exhibited in the SEM images shown in Figures 4A and 4B. At higher magnifications, the nano/micro interface between CNTs and CF can be clearly observed, as the dense CNT forest was grown perpendicularly from the CF surface (Figure 4C).

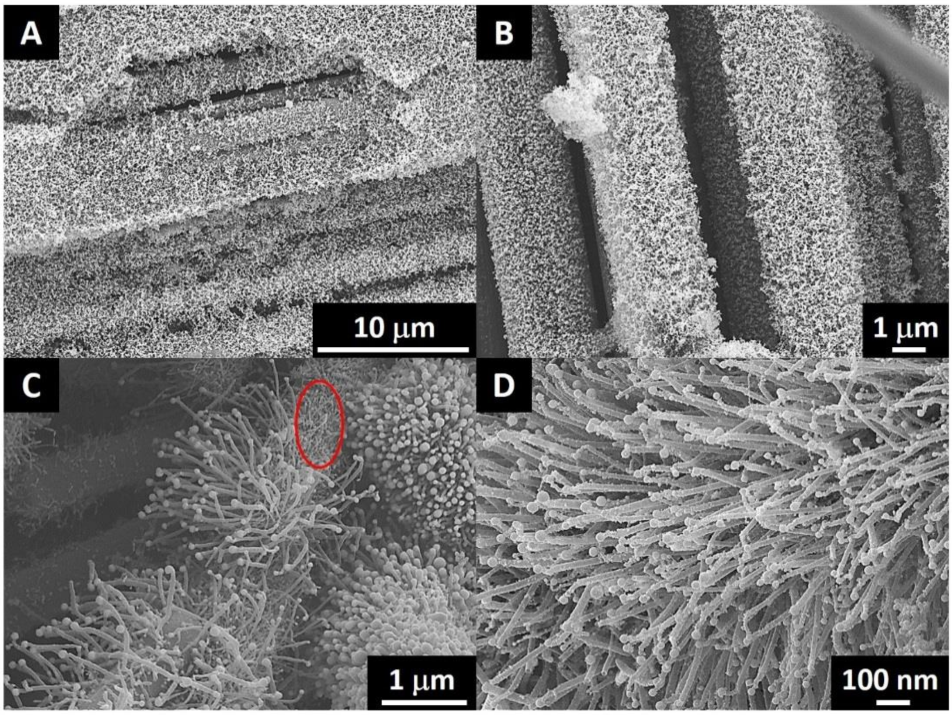

Figure 4:
*SEM images of; **A.-B.** hierarchically structured CNT/CF composites, **C.** CFs covered by the as-grown CNT forest on their surfaces, **D.** zoomed-in view of the marked area in Figure 4C.*

The CNT forest's coverage on the CF fabric surface was high, since the growth was observed to span along the full fiber axis length. Both long-winding and short-rigid CNT types were grown in this forest, indicating the heterogeneous nature of the catalytic growth process induced by MWs Liu et al., (2011). Morphological property details of the as-obtained CNTs were also investigated, and their average diameter was calculated to be ~50 nm while their length could extend up to couple of microns (Figure 4D). The high aspect ratio of these CNTs thus provide an ultra-high surface area, which enables enhanced interfacial interactions and enable multi-scale functions for the composite, through the formation of new interfaces. In good agreement with the relevant previous literature results Poyraz et al. (2013), Xie et al. (2014), Poyraz et al. (2015), the tip-growth mechanism was also effective on the current CNT forest's growth on CF fabric samples. The characteristic matchstick-like morphology, which is composed of hollow and multi-walled stem with oxidized iron nanoparticle (NP) tip, of the as-grown CNTs in this forest (Figure 4D) clearly indicates the effective tip-growth mechanism, as well.

After proving the as-proposed MW-energy based ultrafast CNT growth technique's success on generating CNT/CF hierarchical composites via SEM characterization, the in-depth morphological and elemental features of these structures were further characterized by both TEM microscopy and EDX analysis. Collected results from these analyses are shown in Figure 5. The TEM image in Figure 5A provides more detailed information about the as-grown CNTs by showing their hollow stems that encapsulate catalyst iron NPs. This morphological structure was obtained during the tip-growth process, whose working mechanism would be explained along the following paragraphs. As it also can be seen from the TEM image in Figure 5C, a single ~25 nm × 5 nm iron catalyst NP was encapsulated within the as-grown MWCNTs' wall, which was made up of ultrathin graphene layers. The EDX analysis results of both the as-grown MWCNTs and the encapsulated catalyst iron NPs are shown in Figures 5B and 5D. These diffractograms provide more evidence for the presence of the as-grown MWCNTs and iron NPs that are made up of C and Fe elements, respectively. Also, there are two sharp peaks with Cu indicators in these diffractograms, both of which were caused by the copper grid used for the TEM imaging process as the sample holder.

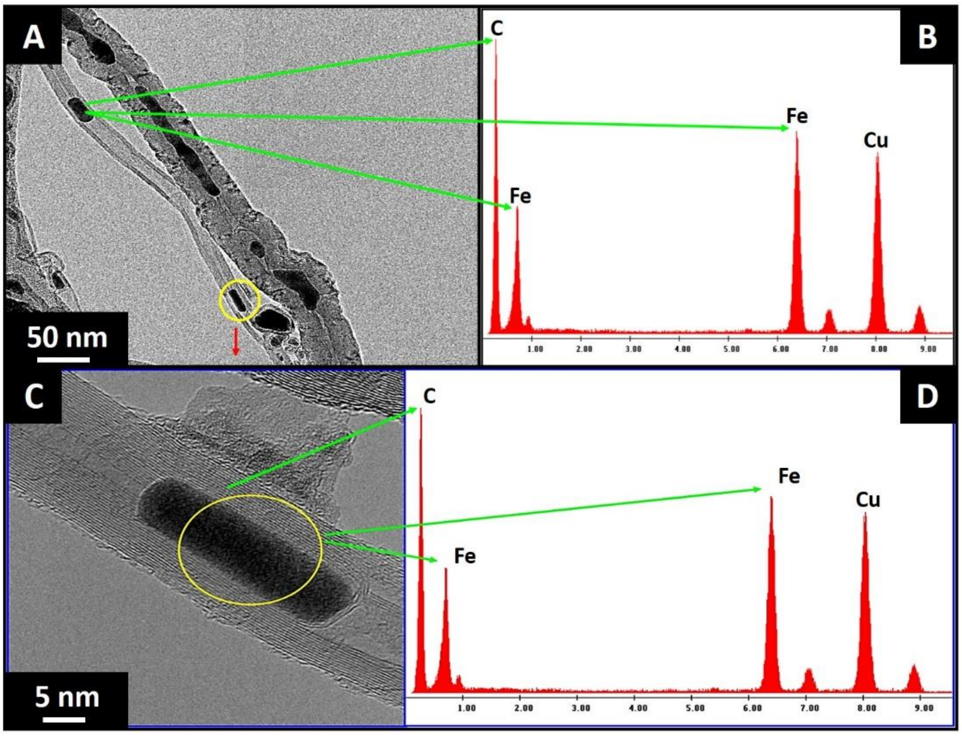

Figure 5:

***A.** TEM image of the catalyst iron NPs encapsulated within the as-grown MWCNTs, **B.** the EDX diffractogram of the catalyst iron NP and the as-grown MWCNT, **C.** HR-TEM image of the marked area in Figure 5A, and **D.** the EDX diffractogram of the marked area in Figure 5C.*

It is thus revealed that the MW-energy assisted ultrafast heating technique was successful on generating CNT/CF nano-micro hierarchical composite structures with high yield and density and within a short period of time. It is strongly believed that the ultrafast CNT growth mechanism on the CF fabric sample surface majorly depends on the high reaction temperature between ferrocene particles and CFs upon MW irradiation. That is to say, as soon as absorbing the MW energy; (i) highly conducting CF fabric sample started sparking and arcing, (ii) then it's surface temperature was rapidly increased above 1000 °C, and (iii) this caused a large amount of heat release within a few seconds. As a result, the fine ferrocene particles on the sample fabric surface got decomposed into its iron and cyclopentadienyl ligands through an instant chain reaction, in gas form. At this point, the iron NPs served as catalysts while the cyclopentadienyl groups were realigned and served as the carbon source for the formation of MWCNTs, respectively Liu et al. (2011), Poyraz et al. (2013), Xie et al. (2014), Poyraz et al. (2015). After all, the dense CNT forest was grown on the CF fabric surface through this liquid-solid-vapor transition mechanism.

4. CONCLUSION

Hierarchical CNT/CF composites with aligned nano-micro interfacial structure were fabricated within seconds by applying MW irradiation. Homogenously grown CNT forest was obtained on the CF fabric surface with high yield, high aspect ratio, and high coverage density. The as-produced hierarchically structured CNT/CF composites offer promising potential for widespread advanced applications including medical applications, supercapacitors, transportation, microelectronics and so on. The as-proposed highly efficient and cost-effective MW energy-assisted fabrication technique also secures the industrial scale production of relevant next generation composites, as well.

REFERENCES

1. Chand, S. (2000) Review carbon fibers for composites, *Journal of Materials Science*, 35(6), 1303-1313. DOI: 10.1023/A:1004780301489
2. Chen, H., Roy, A., Baek, J. B., Zhu, L., Qu, J., Dai, L. (2010) Controlled growth and modification of vertically-aligned carbon nanotubes for multifunctional applications, *Materials Science and Engineering R*, 70, 63-91. DOI: 10.1016/j.mser.2010.06.003
3. Delamar, M., Desarmot, G., Fagebaume, O., Hitmi, R., Pinsonc, J., Saveant, J. M. (1997) Modification of carbon fiber surfaces by electrochemical reduction of aryl diazonium salts: Application to carbon epoxy composites, *Carbon*, 35(6), 801-807. DOI: 10.1016/S0008-6223(97)00010-9
4. Liu, Z., Wang, J., Kushvaha, V., Poyraz, S., Tippur, H., Park, S., Kim, M., Liu, Y., Bar, J., Chen, H., Zhang, X. (2011) Poptube approach for ultrafast nanotube growth, *Chemical Communications*, 47, 9912-9914. DOI: 10.1039/c1cc13359d
5. Poyraz, S., Liu, Z., Liu, Y., Zhang, X. (2013) Devulcanization of scrap ground tire rubber and successive carbon nanotube growth by microwave irradiation, *Current Organic Chemistry*, 17, 2243-2248. DOI: 10.2174/13852728113179990049
6. Poyraz, S., Zhang, L., Schroder, A., Zhang, X. (2015) Ultrafast microwave welding/reinforcing approach at the interface of thermoplastic materials, *ACS Applied Materials and Interfaces*, 7, 22469-22477. DOI: 10.1021/acsami.5b06484
7. Samsur, R., Rangari, V. K., Jeelani, S., Zhang, L., Cheng, Z. Y. (2013) Fabrication of carbon nanotubes grown woven carbon fiber/epoxy composites and their electrical and

mechanical properties, *Journal of Applied Physics*, 113(21), 214903-214908. DOI: 10.1063/1.4808105

8. Thostenson, E., Ren, Z., Chou, T. (2001) Advances in the science and technology of carbon nanotubes and their composites: a review, *Composites Science and Technology*, 61(13), 1899-1912. DOI: 10.1063/1.1466880

9. Thostenson, E. T., Li, W. Z., Wang, D. Z., Ren, Z. F., Chou, T. W. (2002) Carbon nanotube/carbon fiber hybrid multiscale composites, *Journal of Applied Physics*, 91(9), 6034-6037. DOI: 10.1016/S0266-3538(01)00094-X

10. Xie, H., Poyraz, S., Thu, M., Liu, Y., Snyder, E. Y., Smith, J. W., Zhang, X. (2014) Microwave-assisted fabrication of carbon nanotubes decorated polymeric nano-medical platforms for simultaneous drug delivery and magnetic resonance imaging, *RSC Advances*, 4, 5649-5662. DOI: 10.1039/c3ra45913f

11. Xu, B., Wang, X., Lu, Y. (2006) Surface modification of polyacrylonitrile-based carbon fiber and its interaction with imide, *Applied Surface Science*, 253(5), 2695-2701. DOI: 10.1016/j.apsusc.2006.05.044

12. Yu, B., Jiang, Z., Tang, X. Z., Yue, C. Y., Yang, J. (2014) Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating, *Composites Science and Technology*, 99, 131-140. DOI: 10.1016/j.compscitech.2014.05.021

13. Yuan, H., Wang, C., Zhang, S., Lin, X. (2012) Effect of surface modification on carbon fiber and its reinforced phenolic matrix composite, *Applied Surface Science*, 259, 288-293. DOI: 10.1016/j.apsusc.2012.07.034

14. Zhao, Z. G., Ci, L. J., Cheng, H. M., Bai, J. B. (2005) The growth of multi-walled carbon nanotubes with different morphologies on carbon fibers, *Carbon*, 43, 651-673. DOI: 10.1016/j.carbon.2004.10.013