

A Novel Method to Graft Carbon Nanotube onto Carbon Fiber by the Use of a Binder

Huaiping Rong,^{1,2} Keqing Han,¹ Shuang Li,¹ Yingcai Tian,¹ Muhuoyu²

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China

²School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Correspondence to: K. Han (E-mail: hankeqing@dhu.edu.cn)

ABSTRACT: A novel method is developed for grafting multiwall carbon nanotubes (MWNTs) onto the surface of polyacrylonitrile-based high strength (T300GB) carbon fiber. Functionalized MWNTs were well dispersed in the PVA solution and the carbon fiber was dip-coated in this solution. After heat treatment of the coated carbon fiber under a nitrogen atmosphere, MWNTs with carboxyl groups were grafted onto the functionalized carbon fiber via chemical interaction. The resulting materials were characterized by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FESEM), Raman spectrum and mechanical testing. FESEM observations revealed uniform coverage of carbon nanotubes on carbon fiber. The carbon fiber grafted with MWNTs improved the tensile strength by 12% with respect to the pristine carbon fiber. These results are supportive of good interfacial bonding between the carbon nanotubes (CNTs) and carbon fiber. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: carbon fiber; carbon nanotube; poly (vinyl alcohol); nanomaterials

Received 29 October 2011; accepted 11 March 2012; published online

DOI: 10.1002/app.37699

INTRODUCTION

Carbon nanotubes (CNTs) have received considerable attention in the last decade, mainly, because they possess extraordinary properties, and therefore, they have many potential applications.¹ Carbon fiber has been developed as reinforcement for composite materials due to its high specific strength and modulus. These composites are widely used in aerospace, automotive, and sporting goods industries. The introduction of carbon nanotubes on the surface of carbon fiber could help to fill cracks in the fiber and reduce stress concentration, resulting in improved tensile strength of a high strength PAN-based carbon fiber. Oxidative surface modification techniques to improve the adhesion and bonding between the carbon nanotube and carbon fiber have been reported.² Laachachi et al.^{3,4} functionalized CNTs and carbon fiber under acid or thermal treatments to generate oxygen and amine groups, which allow the grafting of CNTs onto a carbon fiber surface by the bonding between CNTs and carbon fiber. Mei et al.⁵ has found a new method to graft CNTs onto the carbon fiber by use of dendrimer. In addition, Zhao et al.⁶ reported using octaglycidyl dimethylsilyl (POSS) as the coupling agent to graft CNTs onto carbon fiber.

In this article, a simple method to graft carbon nanotube onto carbon fiber by dip coating with the PVA/MWNTs solution will be reported. The polar groups attached to the carbon nanotubes increased the dispersibility, which allowed the carbon nanotubes to easily disperse in the PVA solution. PVA acted also as a binder to form a film of PVA with dispersed CNT onto carbon fiber surface. Nath et al.⁷ reported that the PVA under nitrogen at 500°C had burned completely, so the PVA in these experiments should burn from the carbon fiber surface leaving exposed carbon nanotubes. The introduction of MWNTs onto the surface of carbon fiber may help to remedy the surface defects and reduce stress concentrations, resulting in improved tensile strength of the carbon fiber.

EXPERIMENTAL

Materials

Commercially available multiwall carbon nanotubes (MWNTs) (diameter, 10–20 nm; length, 10–30 μm) were supplied from Chengdu Organic Chemicals, Chinese Academy of Sciences. Polyacrylonitrile-based high strength (T300GB) carbon fiber (diameter: 6–9 μm, Toray industry, Japan) was used as raw

© 2012 Wiley Periodicals, Inc.

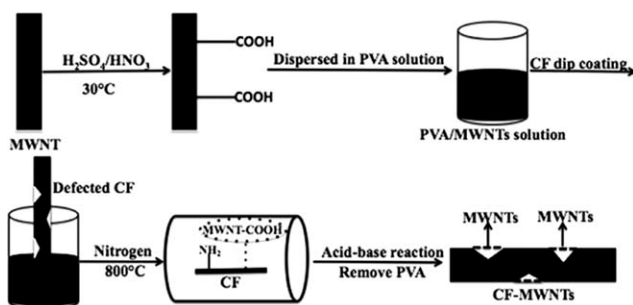


Figure 1. Schematic diagram of procedure for preparing carbon fiber/MWNTs nanomaterials.

materials. Polyvinyl alcohol (average molecular weight: 60,000) was purchased from Shanghai Lanyuan Biological Technology. Concentrated sulfuric acid (98%) and concentrated nitric acid (69%) was obtained from Shanghai Boer Chemical Industry (Shanghai, China). Deionized water and nitrogen with 99.999% purity were also used during sample preparation.

Chemical Treatment of MWNTs

MWNTs were dispersed in a solution of concentrated sulfuric acid and concentrated nitric acid with a 3:1 volume ratio by ultra sonication for 3 h at 30°C. Then the product was separated by centrifuge, washed with deionized water, and dried in a vacuum oven.⁸

Grafting Carbon Nanotubes Onto Carbon Fiber

The procedure of grafting carbon nanotubes on the surface of carbon fiber is shown in Figure 1. 5 g PVA was added to 100 mL deionized water and stirred at 90°C until the PVA was dissolved completely. Then the functionalized MWNTs were added to this solution, and the mixture was ultra sonicated using ultrasonic cell disruptor BILON92-IIID (Shanghai Bilang) for about 2 h in order to get a homogenous solution. The desized carbon fiber was immersed in this solution for 0.5 h, and then was removed before being transferred to the furnace.

The temperature was increased from 25 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere and maintained at 800°C for 30 min. The attached MWNT's weight can be calculated using the coated carbon fiber's weight minus the pristine carbon fiber's weight. The percentage of attached MWNTs can be obtained using the coated MWNT weight divided by the whole weight of carbon fiber.

Characterization

Fourier transform infrared (FTIR) spectra of samples in KBr pellets were obtained by a Nicolet 8700 spectrometer with a resolution of 4 cm⁻¹. For the FTIR spectra of MWNT, MWNTs were mixed with the KBr with the mass ratio of 1:100. For the FTIR spectra of carbon fiber, the fiber was cut and grind into the power with the KBr. X-ray photoelectron spectroscopy (XPS) was carried out to examine the elements and functional groups of the carbon fiber surface using a Surface Science Laboratories SSX-100 ESCA spectrometer with monochromatic Al K α radiation (1486.6 eV). Fiber morphologies were revealed by field emission scanning electron microscopy (FESEM) using a Hitachi S-3000N instrument. Raman spectra were recorded in the range of 500–4000 cm⁻¹ at ambient temperature using a WITEC Spectra Pro 2300I spectrometer equipped with an Ar-ion laser, which provided a laser beam of 488 nm wavelength.

The tensile specimens were tested according to ISO 11566 at room temperature and at a cross head speed of 5 mm/min using a Universal Tensile Machine (WDW-20, Shanghai, China), leaving approximately 25-mm gauge length. At least 10 samples were tested in order to get a good statistics of measured values.

RESULTS AND DISCUSSION

Characterization of MWNTs and Carbon Fiber by FTIR

The FTIR spectra of pristine MWNTs and functionalized MWNTs were shown in Figure 2. In Figure 2(a), OH absorptions appeared at 3400 cm⁻¹, while the bands at 2850 cm⁻¹ and 2920 cm⁻¹ were assigned to hydrocarbon groups (—CH_x). In

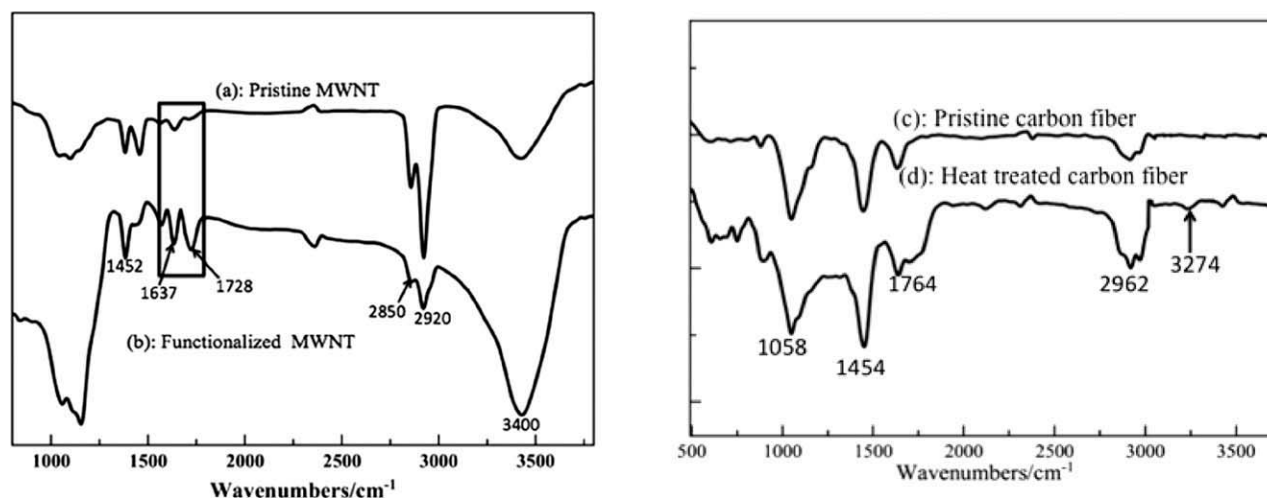


Figure 2. FTIR spectra of MWNTs and carbon fiber: (a) pristine MWNTs, (b) functionalized MWNTs, (c) pristine carbon fiber and (d) carbon fiber after heat treatment under nitrogen.

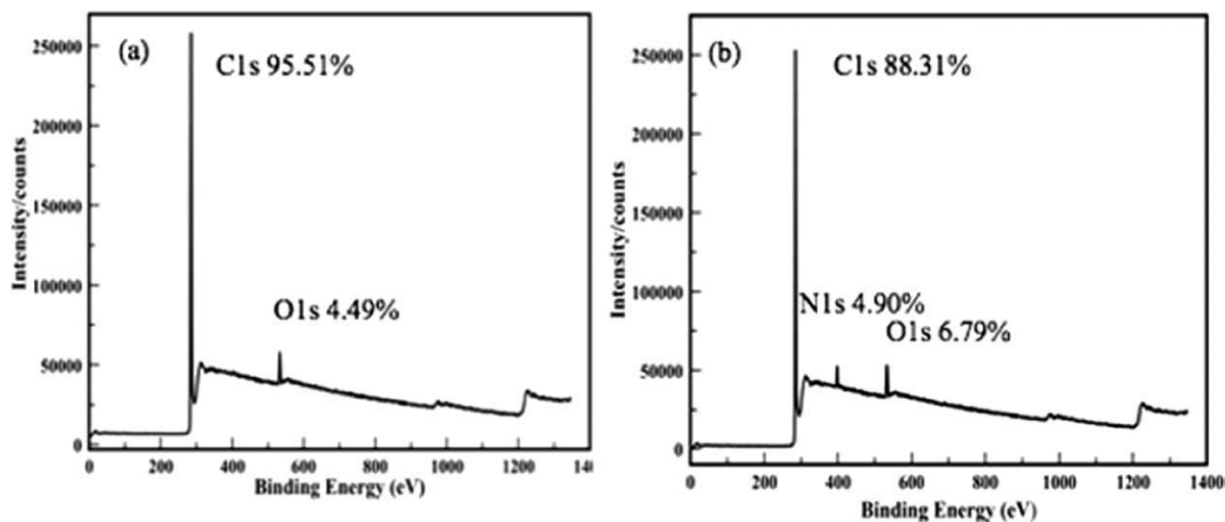


Figure 3. XPS wide scan spectra of functionalized carbon fiber: (a) pristine carbon fiber and (b) carbon fiber after heat treatment under nitrogen.

Figure 2(b), acid-functionalized MWNTs appeared a peak at 1728 cm^{-1} , which was assigned to the $\text{C}=\text{O}$ functional group; therefore, $-\text{COOH}$ groups must have been generated on the MWNTs from the chemical treatment with the concentrated acid mixture.^{3,9} After being exposed to elevated temperatures, chemical bonding was formed on the carbon fiber surface, which was confirmed by FTIR data in Figure 2. The FTIR spectra of the carbon fiber in Figure 2(c) showed it had not shown us the $\text{N}-\text{H}$ group, just some $\text{C}-\text{C}$ stretch group. For the nitrogen heat-treated carbon fiber [Figure 2(d)], the FTIR spectrum mainly include one peak located at 3274 cm^{-1} , which was allotted to $\text{N}-\text{H}$, this was a big difference from the Figure 2(c). When MWNT were grafted onto the carbon fiber, the increase of the band at around 1760 cm^{-1} was attributed to the anhydride $\text{C}=\text{O}$, because of the carboxyl groups on the carbon nanotube surface.¹⁰

Characterization of Functionalized Carbon Fiber by XPS

Figure 3(a, b) showed the typical XPS spectra of the carbon fiber before and after heat treatment under nitrogen. As shown in Figure 3(a) the only C1s and O1s were visible, which was as we expected. However, after the carbon fiber heat-treated under nitrogen, besides C1s and O1s peaks, N1s came forth, as demonstrated in Figure 3(b), indicating the existence of amino

groups on the carbon fiber surface. XPS and FTIR spectra demonstrated that carbon nanotubes and carbon fibers were functionalized under acid and thermal treatment, respectively, leading to the generation of surface carboxyl and amino groups. These functional groups could further react to form chemical bonds between nanotubes and carbon fiber during the thermal treatments.

Fiber Morphology

SEM investigations have been carried out to show the surface morphology of the carbon fiber. It has lots of bubbles and cracks on the carbon fiber surface. So pristine carbon fibers had defects on its surface [Figure 4(a)]. After dipping the carbon fiber into PVA/CNTs suspension, the air-dried PVA/CNT film was formed on the carbon fiber surface [Figure 4(b)]. After the PVA/MWNT film was formed on the carbon fiber surface, the carbon fiber was transferred into a furnace. The temperature of the furnace was increased to 800°C at the rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. After that the furnace had cooled down to room temperature, the PVA was completely burned from the carbon fiber surface leaving exposed carbon nanotubes [Figure 4(c)].

Figure 5 showed the surface morphology of the carbon fiber grafted with the MWNTs. It was confirmed by FESEM images

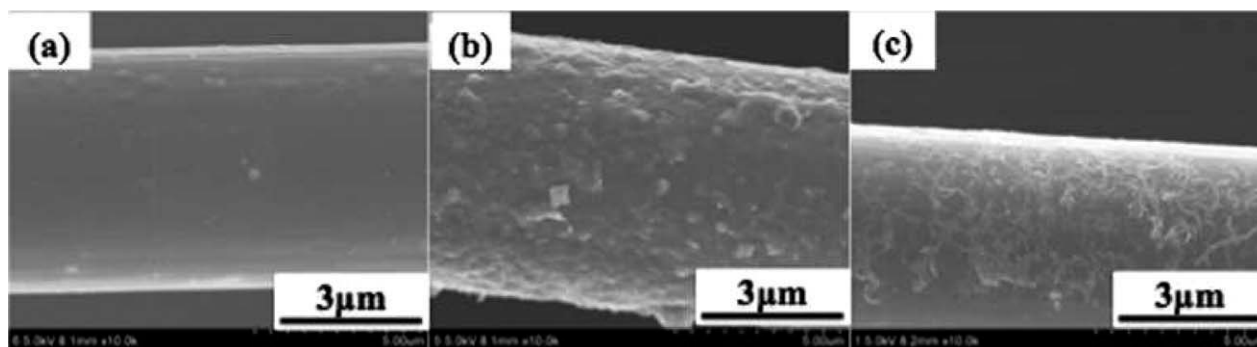


Figure 4. FESEM images of carbon fiber (a, Pristine carbon fiber; b, carbon fiber dipped in the PVA solution; c, carbon fiber removed from the PVA).

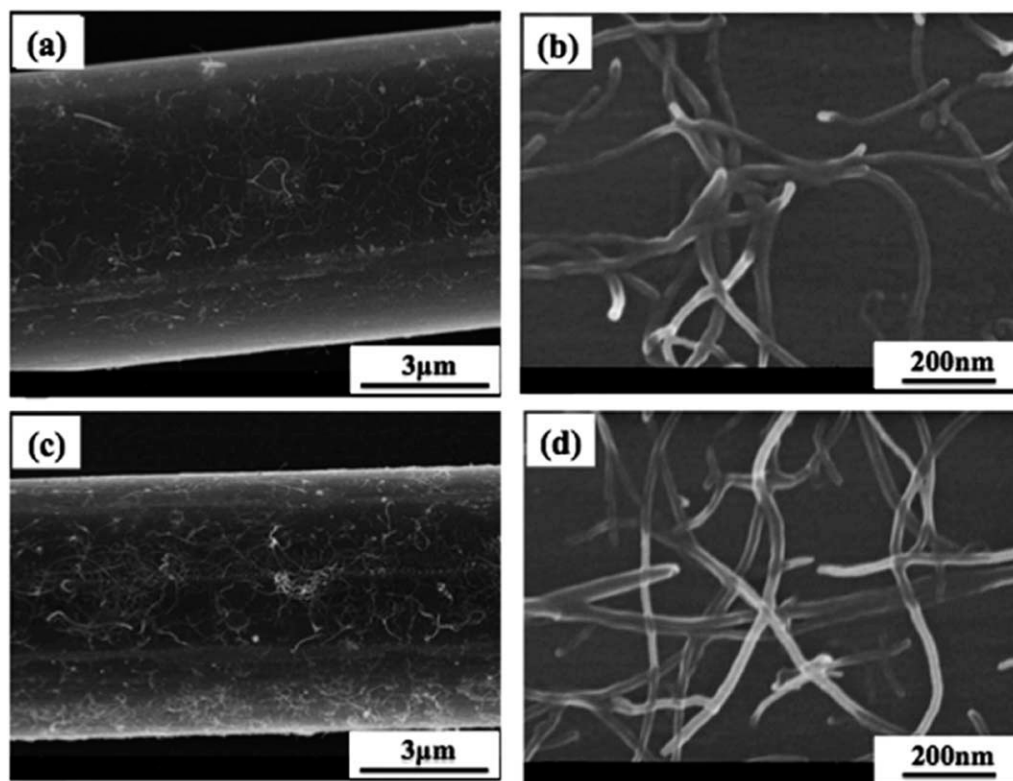


Figure 5. FESEM images of carbon fiber grafted with carbon nanotube (a-b: at a PVA/MWNTs mass ratio of 20:1, c-d: at a PVA/MWNTs mass ratio of 10:1).

that MWNTs were uniformly attached on the carbon fiber surface. Carboxyl groups were generated on MWNTs after chemical treatment with the concentrated acid mixture. Because of the high temperature process in nitrogen atmosphere, PVA was removed by pyrolysis from the carbon fiber surface exposing only the carbon nanotubes. The percentage of attached MWNTs can be controlled by the mass ratio of PVA to MWNTs. At a

PVA/MWNTs mass ratio of 20:1 [Figure 5(a, b)] the percentage of attached MWNTs was about 5%, while at a PVA/MWNTs mass ratio of 10:1 [Figure 5(c, d)] the percentage of attached MWNTs was nearly 12%. The introduction of MWNTs nano-coating on the surface of carbon fiber could help to “heal” cracks and reduce stress concentrations, resulting in improved tensile strength of a high strength PAN-based carbon fiber.

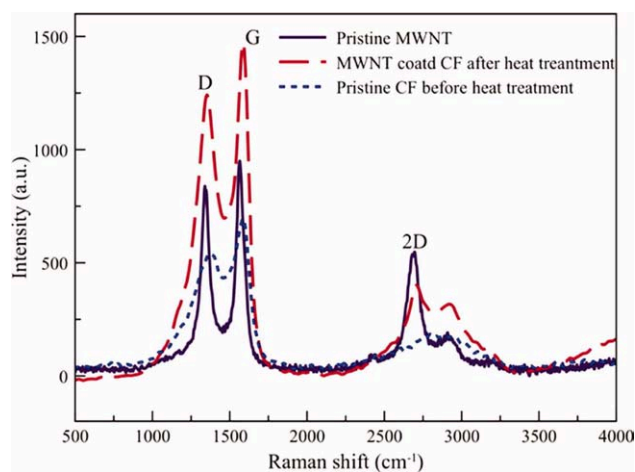


Figure 6. Raman spectra of pristine MWNT; pristine carbon fiber with some defect; MWNT coated carbon fiber after heated treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

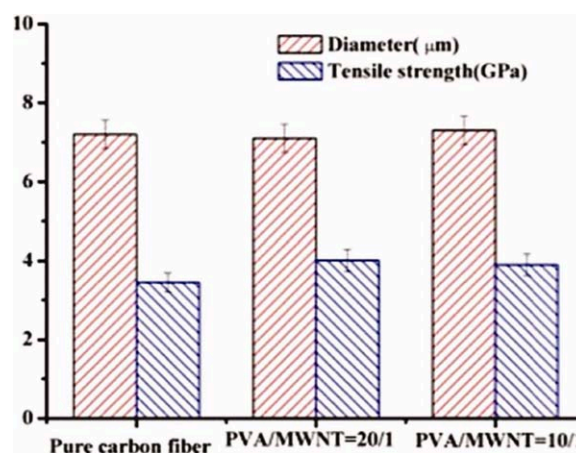


Figure 7. Mechanical properties of carbon fiber/MWNTs nanomaterial. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of the Composite by Raman Spectra

The Raman spectra for the pristine MWNT; pristine carbon fiber before heat treatment and MWNT-coated carbon fiber after heat treatment were shown in Figure 6. It was clearly seen that the two bands around 1580 cm^{-1} and 1350 cm^{-1} in the spectra were assigned to the tangential mode (*G* band) for the stretching vibrations of sp^2 carbon atoms and the disorder mode (*D* band) induced by sp^3 hybridization, respectively.¹¹ A low $I_{D/G}$ values is generally attributed to the presence of less structure defects.¹² For pristine carbon fiber before heat treatment, the $I_{D/G}$ equaled to 0.80, but when MWNT-coated carbon fiber after heat treatment, the $I_{D/G}$ equaled to 0.74. It is demonstrated that MWNTs attached to the surface of carbon fiber could help to remedy the existing defects. The second harmonic peak of the 2D band at 2700 cm^{-1} , historically named the *G'* band, was observed, and it was much higher in case of MWNTs grafting carbon fibers than the bare carbon fibers.

Tensile Strength of the Nanomaterials

The tensile strength of carbon fiber with and without grafted MWNTs, and with different mass ratio of PVA to MWNTs was tested, respectively. Figure 7 lists the mechanical properties of carbon fiber/MWNTs nanomaterials and compared with the as received carbon fiber. The tensile strength of the carbon fiber/MWNTs nanomaterials was enhanced with increasing MWNTs content. When the mass ratio of PVA to MWNTs was 10:1, the tensile strength of carbon fiber/MWNTs increased by about 21% than that of as received carbon fiber. From the SEM we know that the as received carbon fiber surface had lot of defects [Figure 4(a)]. This may led to stress concentrations and to a decrease of the tensile strength of carbon fibers. The introduction of MWNTs on the surface of carbon fiber helps to “fill” the cracks on the fibers surface and therefore reduce stress concentrations, resulting in improved tensile strength of carbon fiber.

CONCLUSIONS

A simple method for grafting MWNTs onto the surface of carbon fiber was reported. The carbon fiber was dip-coated with PVA/functionalized MWNTs solution and then subjected to the thermal treatments, leading to form chemical bonds between the CNTs and carbon fiber. FESEM images revealed that MWNTs were uniformly grafted onto the carbon fiber surface. The tensile strength of carbon fiber grafted with MWNTs nanocoating increased by average 12% with highest up to 21%

compared with carbon fiber that did undergo similar thermal treatments. The introduction of MWNTs onto the surface of carbon fiber could help to remedy the surface defects and reduce stress concentrations, resulting in the tensile strength of carbon fiber. The results clearly demonstrated that the excellent dispersion of MWNTs on the surface of carbon fiber and a strong interfacial bonding with the carbon fiber were effective in improving the tensile strength of carbon fiber.

ACKNOWLEDGMENTS

This work is supported by the National Basic Research Program (Grant No. 2011CB605600-G) of China (973 Program) and also is supported by the Ph.D. Students Innovation Project of Donghua University Shanghai city in China (Grant No. 9D10628).

REFERENCES

1. Iijima, S. *Nature* **1991**, *354*, 56.
2. Carrión, F. J.; Sanes, J.; Bermúdez, M.-D.; Arribas, A. *Tribol. Lett.* **2010**, *41*, 199.
3. Laachachi, A.; Vivet, A.; Nouet, G.; Ben Doudou, B.; Poilane, C.; Chen, J.; Bai, J. B.; Ayachi, M. *Mater. Lett.* **2008**, *62*, 394.
4. Pittman, C. U.; He, G. R.; Wu, B.; Gardner, S. D. *Carbon* **1997**, *35*, 317.
5. Mei, L.; He, X. D.; Li, Y. B.; Wang, R. G.; Wang, C.; Peng, Q. Y. *Mater. Lett.* **2010**, *64*, 2505.
6. Zhao, E.; Huang, Y. D. *J. Mater. Chem.* **2011**, *21*, 2867.
7. Nath, D.C. D.; Sahajwalla, V. *Appl. Phys. A* **2011**, *104*, 539.
8. Kim, I. T.; Nunnery, G. A.; Jacob, K.; Schwartz, J.; Liu, X. T.; Tannenbaum, R. J. *Phys. Chem. C* **2010**, *114*, 6944.
9. Kitano, H.; Tachimoto, K.; Anraku, Y. J. *Colloid Interface Sci.* **2007**, *306*, 28.
10. Cha, B. J.; Kang, Y. S.; Won, J. *Macromolecules* **2001**, *34*, 6631.
11. Luo, Y.; Zhao, Y.; Cai, J.; Duan, Y.; Du, S. *Mater. Des.* **2011**, *33*, 405.
12. Kim, H. J.; Bae, M. J.; Kim, Y. C.; Cho, E. S.; Sohn, Y. C.; Kim, D. Y.; Lee, S. E.; Kang, H. S.; Han, I. T.; Kim, Y. H.; Patole, S. P.; Yoo, J. B. *Nanotechnology* **2011**, *22*, 095602.