MODIFIED SINGLE-WALL CARBON NANOTUBES FOR REINFORCE THERMOPLASTIC POLYIMIDE

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ABSTRACT

A significant improvement in the mechanical properties of the thermoplastic polyimide film was obtained by the addition of noncovalently functionalized single-wall carbon nanotubes (SWNTs). Polyimide films were reinforced using pristine SWNTs and functionalized SWNTs (F-SWNTs). The tensile strengths of the polyimide films containing F-SWNTs were found to be approximately 1.4 times higher than those prepared from pristine SWNTs.

KEY WORDS: Polyimide (PI), Nanocomposites

1. INTRODUCTION

A number of theoretical and experimental studies confirm that single-wall carbon nanotubes (SWNTs) possess extraordinary mechanical, electrical, and chemical properties (1-10). Their excellent strength, stiffness, stability and high conductivity (both thermal and electrical) are due to the perfect alignment of the carbon atomic lattice along the tube axis and their closed topology (11). The outstanding properties observed in SWNTs offer advantages over many conventional materials (e.g., carbon fibers), not only because they have superior properties, but also because SWNTs have a large surface area (i.e., 285 m^2/g for SWNTs ropes; the total outer surface area of the individual tubes is about 1300 m^2/g) which could be very useful for mechanical and chemical applications (11-12). The intrinsic properties of SWNTs make them ideal materials for use in aerospace and space exploration. Their high modulus (100 times that of steel at one-sixth of the density) and low weight make SWNTs excellent reinforcements for composite materials which could be used to fabricate lightweight components for vehicle structures and other space systems, e.g., habitats and large area platforms.

Numerous polymers, including epoxy resins, have been used to prepare carbon nanotube/polymer composites with the aim of enhancing the mechanical, thermal, and electrical properties of the composite (13-24). An important requirement for the effective use of SWNTs as reinforcements in structural materials is the ability to manipulate them. Stable SWNT suspensions could be used to form a homogeneous distribution of nanotubes in a given matrix resin, essential for an effective and strong load transfer between the carbon nanotubes and the polymer matrix to enable the desired strength improvements.

The addition of functionalized SWNTs to polymer matrices has been shown to improve the dispersibility and the interfacial compatibility between the polymer and SWNTs as compared to material system prepared using unfunctionalized SWNTs. For example, Mitchell and co-worker

prepared SWNTs functionalized with 4-(10-hydroxy)decyl benzoate to investigate the viscoelastic properties of the resulting polystyrene nanocomposite (25). Based on the viscoelastic properties of these nanocomposites, they found that the reinforcement and the degree of dispersion were much improved when using the functionalized SWNTs in polystyrene. Fluorinated SWNTs have also been used as filler for composites. The storage modulus was found to increase by about a factor of four (from 0.3 GPa to 1.2 GPa) when 4 wt % of fluorined SWNTs was added to poly(ethyleneoxide) (PEO) matrix using a roll-cast system (15). Other research and development groups have used surfactants to disperse improvement of the SWNTs. For example, Zhang and co-workers initially dispersed SWNTs in water using sodium dodecyl sulfate (SDS) and then added poly(vinyl pyrrolidone) (PVP) to obtain PVP-wrapped SWNTs. These were then incorporated into polyvinyl alcohol (PVA) (26). The resulting PVA/PVP/SDS/SWNT composite containing 5 wt % SWNTs (with respect to the PVA) exhibited a 78% increase in tensile strength in comparison with the neat PVA film (from 83 MPa to 148 MPa) (26).

In this work we report a simple way to synthesis noncovalently functionalized SWNTs (F-SWNTs) utilizing a polycyclic aromatic hydrocarbon based amide and discuss the effect of adding F-SWNTs on the tensile strengths of thermoplastic polyimide films.

2. EXPERIMENTAL

2.1 Materials Crude single-walled carbon nanotubes (SWNTs) obtained for this study were synthesized at Rice University using the high pressure CO disproportionate (HiPCO) process (27). The SWNTs were purified in grams quantities by a modified heat/oxidative technique that minimized the iron content of HiPCO SWNTs from 35-40 wt % to less than 0.05 wt % (28).

o-Chlorobenzene (OCB), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrahydrofuran (THF), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), methanol, ethanol, thionyl chloride ($SOCl_2$), triethylamine, sodium carbonate (Na_2CO_3) and sodium sulfate ($NaSO_4$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) and nitric acid (HNO_3) were purchased from Fisher. The 1-pyrenebutanoic acid used in this study was purchased either from Molecular Probes or Sigma-Aldrich. 2,2-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP) was purchased from the Wakayama-Seika-Kogyo Company. Bisphenol-A-dianhydride (BPADA) was purchased from GE Plastics.

2.2 Measurements Infrared (FT-IR) spectra were measured in a KBr pellet using a Nicollet Model 510p Spectrometer. Ultraviolet-visible (UV-vis) spectra were measured on solutions, solvent as indicated, with a Shimadzu Model UV-3101PC Spectrometer, using 10-mm light path cell from Apple Scientific, Inc.

The mechanical properties were determined using an Instron Model 4505 machine using the series IX data acquisition software. At least six samples were measured for each film cut in a type V dog-bone specimen, as described in ASTM D882.

2.3 Synthesis

2.3.1 1-Pyrene-(4-(N-5-Norbornene-2,3-Dicarboximide)Benzene)Butanamide (1) **Step A:** 1-Pyrenebutanoic acid (1.0 g, 3.47 mmol) followed by 5-10 mL of $CHCl_3$ were added to a 50-mL three-necked round bottom flask equipped with a condenser and magnetic stirrer. Thionyl chloride ($SOCl_2$) (0.38 mL, 5.20 mmol, 1.5 equiv) was added to this suspension and the resulting mixture was refluxed for 2 h. (Note: 2 h is the maximum time of reaction reflux; longer times tended to decrease the product yield.) The reaction solution was cooled to room temperature and then transferred carefully with a pipette to a single neck round bottom flask to remove the solvent and the $SOCl_2$ excess by vacuum distillation. (Addition of small portion of tetrahydrofuran helped to completely eliminate the $SOCl_2$.) The brownish-yellow 1-pyrene butanoylchloride was used in step B without further purification.

Step B: A solution of 4-(*N*-5-norbornene-2,3-dicarboximide)-1-aminobenzene (0.53 g, 3.26 mmol), 0.45 mL of triethylamine in 5 mL of $CHCl_3$ were added under nitrogen atmosphere to a two-necked round bottom flask equipped with a condenser. The reaction was cooled to 0 ºC in an ice bath. A solution of crude 1-pyrenebutanoyl chloride in about 5 mL $CHCl_3$ was carefully added and the reaction mixture was stirred overnight. The reaction mixture was then transferred to a separator funnel and washed first with 5% HCl (2 x 25 mL), and then with an aqueous Na_2CO_3 (1 x 10 mL) solution. The organic phase was dried over $NaSO_4$, filtered and concentrated under vacuum. (Note: When the product is obtained as a "fluffy" solid, it is re-dissolved in a minimum amount of $CHCl_3$, transferred to a beaker, slowly air-dried, and then placed in a vacuum oven at 65 ºC to completely remove the solvent). The product obtained was a yellow solid in typical reaction yields of about 65%. ^{1}H NMR (200 MHz, $CDCl_3$/TMS,): 1.38 (d, J = 23.8 Hz, 1H, -CH), 1.63 (d, J = 23.8 Hz, 1H, -CH), 2.04-2.31 (m, 4H, -CH), 3.20 (d, J = 67.6 Hz, 6H, -CH$_2$), 6.13 (s, 2H, HC=CH), 6.91 (d, J = 26.2 Hz, 2H, Ar-H), 7.41 (d, J = 29.0 Hz, 2H, Ar-H), 7.56-8.27 (m, 9H, Ar-H).

2.3.2 Bisphenol-A-Dianhydride (BPADA)/Bisphenol-A-Dianhydride (BAPP) Thermoplastic Polyimide (2) A 250-mL round bottom flask equipped with a condenser was flame-dried under flowing nitrogen. BPADA (10.0 g, 19.2 mmol) was mixed with BAPP (7.88 g, 19.2 mmol) in anhydrous NMP (115 mL, 15 wt % solid). The solution was stirred overnight at room temperature, and then refluxed for 4 h. The viscous solution was diluted with 30-60 mL NMP, and precipitated into ethanol. The precipitate was collected and dried in a vacuum oven, overnight at 40 ºC. The dried polymer fibers were then dissolved in CH_2Cl_2 and precipitated in ethanol. The polymer fibers were collected and dried in a vacuum oven, overnight at 40-55 ºC.

2.3.3 Noncovalent Functionalization of SWNTs (F-SWNTs) Dimethylformamide (DMF) (10 mL) was added to the purified HiPCO SWNTs (0.050 g) and the resulting mixture was ultra-sonicated for 30 minutes. Compound **1** (0.200 g, 0.38 mmol), dissolved with 10 mL of DMF was added and the mixture was placed in the refrigerator (0 ºC) for 24 h. The suspension was then centrifuged for 30 minutes and the supernatant removed with a pipette leaving the F-SWNTs in the bottom of the vial.

The F-SWNTs were washed with cold DMF (20 mL) until the compound **1** was not detected in the solvent. The solution was well shaken and centrifuged each time. The F-SWNTs were then

washed with cold methanol (20 mL), the solution was again well shaken, centrifuged for about 20 minutes, the supernatant removed and finally dried in a vacuum oven at room temperature to a constant weight.

2.3.4 Thermoplastic Polyimide Films Reinforced with SWNTs or F-SWNTs General procedure: Polyimide **2** (1 g) was dissolved in about 10 mL of DMF/NMP (4:1). Then, the solution was mixed with the carbon nanotubes material, already dispersed in DMF/NMP (4:1). The final solution was poured into a Petri dish, and heated overnight in a high vacuum oven at 65 ºC. The temperature was then increased to 125 ºC to complete the removal of the solvent.

3. DISCUSSION AND RESULTS

3.1 Noncovalent Functionalization Single Wall Carbon Nanotubes (F-SWNTs) F-SWNTs were prepared by adding SWNTs to a DMF solution of compound **1** as described in the Experimental section. Compound **1** contains a terminal nadic ester (NE) which is commonly used as a reactive end-cap in high temperature polyimides (29). Treatment of a suspension of SWNTs in a DMF solution containing pyrene **1** produced nanotube/pyrene -complexes (F-SWNTs) which form a very stable colloidal suspension in DMF (Figure 1). The highly aromatic pyrene moiety leads to strong π–π interactions with the SWNTs. At the same time the polar amide tail of **1** interacts well with the solvent leading to the observed stable suspension. F-SWNTs can be dispersed in DMF in about 10 minutes or less using a water bath sonicator.
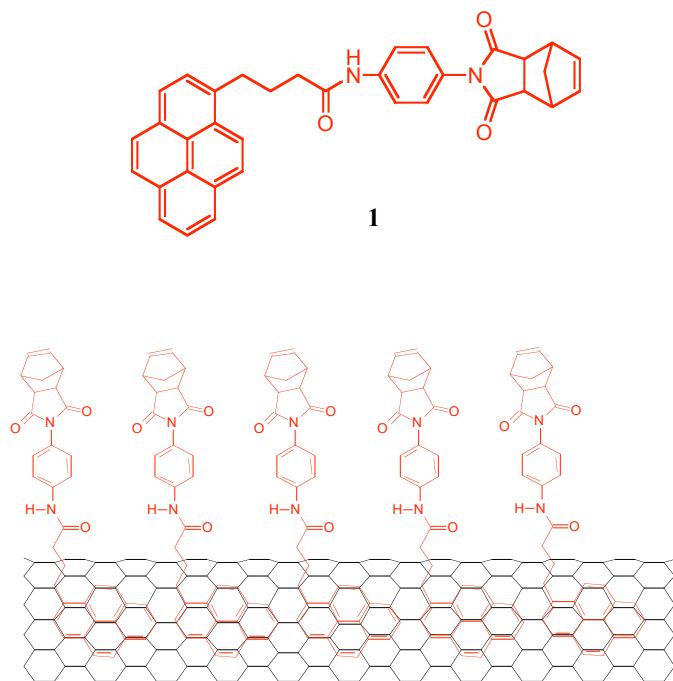

1

Figure 1. Schematic illustration of noncovalent sidewall F-SWNTs via π-π interaction with compound **1**

The FT-IR spectra of the SWNTs before and after noncovalent functionalization with compound **1** are shown in Figure 2. The FT-IR spectrum, after functionalization, shows a carbonyl band at 1704 cm^{-1} similar to that found in the infrared spectrum of compound **1** (Figure 1c). This demonstrates the presence of **1** with the SWNTs and indicates the formation of SWNT/compound **1** adduct.
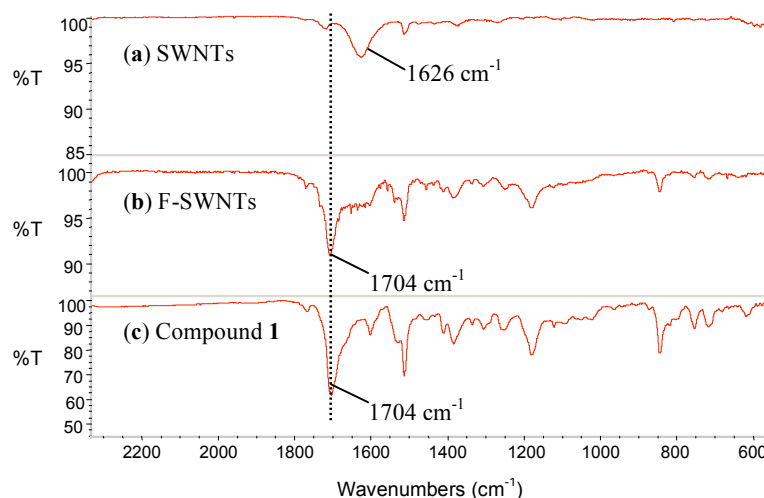

Figure 2. FT-IR spectrum of SWNTs before (**a**) and after (**b**) noncovalent functionalization with compound **1** (**c**)

The UV-vis absorption spectra of SWNTs before and after noncovalent functionalization (1 mg of the SWNTs sample in 10 mL of OCB) show van Hove bands characteristic of carbon nanotubes (Figure 3). Van Hove bands are related to band gap transitions, mainly of the semi-conducting SWNTs. However the intensity of these van Hove bands is decreased after functionalization, suggesting that the π system of the carbon nanotubes may be perturbed by interactions with the pyrene moiety of compound **1** present on the SWNTs surface (30-37).
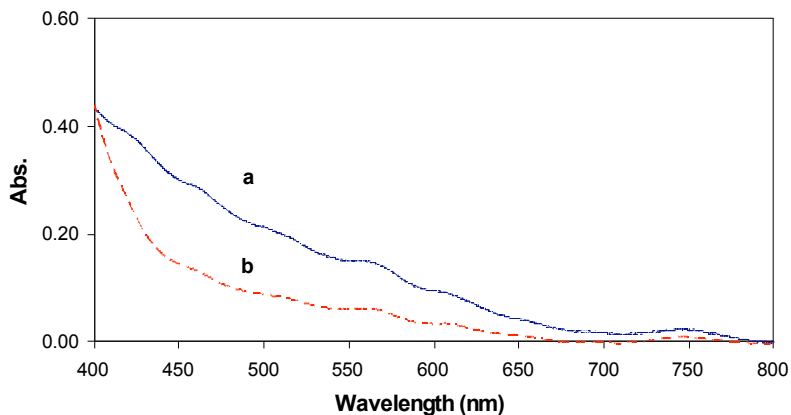

Figure 3. UV-vis spectra of SWNTs before (**a**) and after (**b**) noncovalent functionalization

5

Thermoplastic polyimide BPADA/BAPP (**2**) nanocomposites containing either SWNTs or F-SWNTs were prepared. The bar chart in Figure 4 shows the tensile strength obtained for films made with these polyimide nanocomposites. Each data entry for the tensile strength represents an average value obtained from testing six nanocomposite film samples (cut from a large cast nanocomposite film). Although, the SWNTs were well suspended in the polymeric solution, there was little control in the final homogeneity of the SWNTs throughout the cast film.
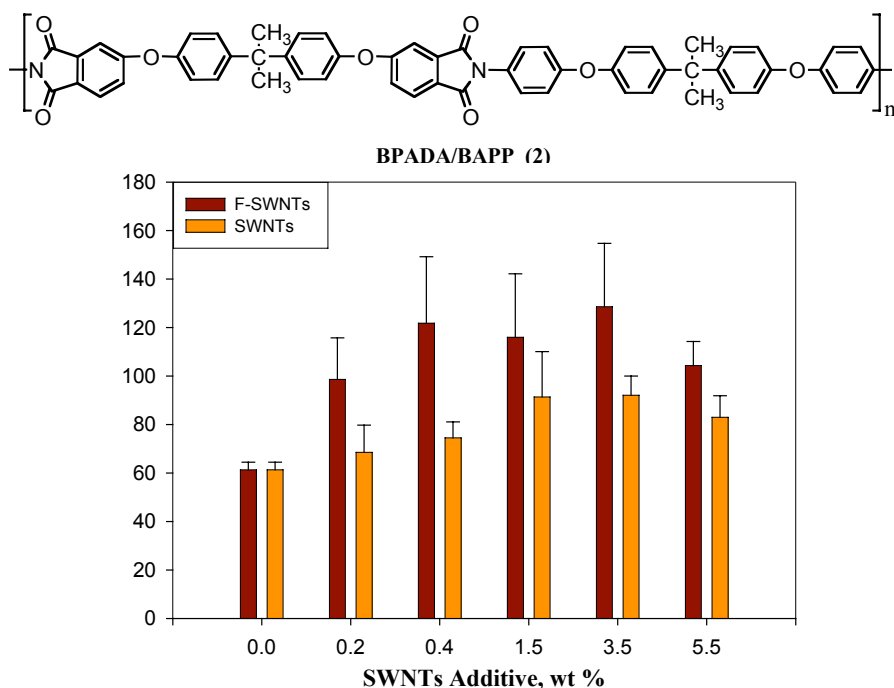

BPADA/BAPP (2)

Figure 4. Effect of addition of functionalized or nonfunctionalized SWNTs on the tensile strength of a polyimide film

Addition of either SWNTs or F-SWNTs increased the tensile strength of the polyimide film; however, those with F-SWNTs had a larger change on the tensile strength possessed the largest increase. Addition of 3.5 wt % of the noncovalently functionalized SWNTs increased the tensile strength from 61.35 MPa (neat polyimide) to 128.60 MPa - an improvement of about 109%.

During the casting process the F-SWNTs do not tend to agglomerate to the extent observed with non-functionalized SWNTs. The observed greater improvements in the tensile strength of films prepared with F-SWNTs are due to the improved dispersions obtained with functionalization which prevents agglomeration of the tubes during the casting process. In addition, the presence of the amide functionality on surface of the F-SWNTs should also enhance chemical interactions between the nanotubes and the matrix, thereby leading to a stronger interface and better tensile properties.

4. CONCLUSION

In summary, it was shown that noncovalent functionalization allows more efficient dispersion of the purified single-wall carbon nanotubes in a thermoplastic polyimide matrix. This resulted in a substantially greater increase in the tensile strength of the polymeric film. At low loading levels of functionalized carbon nanotubes, the tensile strength increased in a linear fashion with increasing nanotube content. At higher loading levels the mechanical properties dropped off with increasing carbon nanotube content, however, the resultant tensile strength was still significantly higher than that of the neat polyimide film.

These enhancements obtained with the addition of functionalized single-wall carbon nanotubes are very encouraging because they demonstrate a significantly improve in the strength properties of the polymer matrix. The improvements in material strength properties demonstrated in this work, coupled with previous work which indicated the possibility of controlling the electrical conductivity (13-26). Use of these SWNT/polymer nanocomposites in aerospace vehicles will enable substantial reductions in component weight.

5. REFERENCES

1. R. S. Ruoff and Lorents, D. C., Carbon, 33, 135 (1995).
2. N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett., 68, 1579 (1992).
3. B. I. Yakobson, P. Avouris, M. S. Dresselhaus and G. Dresselhaus, eds., Carbon Nanotubes: Synthesis, Structure, Properties, and Applications, Springer-Verlag Berlin Heidelberg, New York, 2001, pp. 299-302.
4. D. H. Robertson, D. W. Brenner and J. W. Mintmire, Phys. Rev. B, 45, 12592 (1992).
5. B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett., 76, 2511 (1996).
6. C. F. Cornwell and L. T. Wille, Solid State Commun., 101, 555 (1997).
7. E. Hernández, C. Goze, P. Bernier and A. Rubio, Phys. Rev. Lett., 80, 4502 (1998).
8. C. Dekker, Phys. Today, 22, (1999).
9. A. Krishnan, E. Dujardin, T. W. Ebbesen, P. N. Yianilos, M. M. J. Treacy, Phys. Rev. B, 58, 14013 (1998).
10. J.-P. Salvetat, J.-M. Bonard, N. H. Thomson, A. J. Kulik, L. Forró, W. Benoit and L. Zuppiroli, Appl. Phys. A, 69, 255 (1999).
11. P. M. Ajayan, Chem. Rev., 99, 1787 (1999).
12. Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith and R. E. Smalley, Appl. Phys. Lett., 74, 2307 (1999).
13. R. Haggenmueller, H. H. Gommans, A. G. Rinzler, J. E. Fischer and K. I.Winey, Chem. Phys. Lett., 330, 219 (2000).
14. D. Quian, E. C. Dickey, R. Andrews and T. Rantell, Appl. Phys. Lett., 76, 2868 (2000).
15. X. Zhang, T. Liu, T. V. Sreekumar, S. Kumar, V. C. Moore, R. H. Hauge and Smalley, R. E., Nano Lett., 3, 1285 (2003).
16. M. S. P. Shaffer and A. H. Windle, Adv. Mater., 11, 937 (1999).
17. C. Bower, R. Rosen, L. Jin, J. Han and O. Zhou, Appl. Phys. Lett., 74, 3317 (1999).
18. L. Jin, C. Bower and O. Zhou, Appl. Phys. Lett., 73, 1197 (1998).
19. J. Sandler, M. S. P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte and A. H. Windler, Polymer, 40, 5967 (1999).

20. J. K. W. Sandler, J. E. Kirl, I. A. Kinloch, M. S. P. Shaffer and A. H. Windle, <u>Polymer</u>, <u>44</u>, 5893 (2003).

21. P. M. Ajayan, O. Stephan, C. Colliex and D. Trauth, <u>Science</u>, <u>265</u>, 1212 (1994).

22. L. S. Schadler, S. C. Giannaris and P. M. Ajayan, <u>Appl. Phys. Lett</u>., <u>73</u>, 3842 (1998).

23. O. Lourie, D. M. Cox and H. D. Wagner, <u>Appl. Phys. Lett</u>., <u>73</u>, 3527 (1998).

24. H. D. Wagner, O. Lourie, Y. Feldman and R. Tenne, <u>Appl. Phys. Lett</u>., <u>72</u>, 188 (1998).

25. C. A. Mitchell, J. L. Bahr, S. Arepalli, J. M. Tour and R. Krishnamoorti, <u>Macromolecules</u>, <u>35</u>, 8825 (2002).

26. H. Geng, R. Rosen, B. Zheng, H. Shimoda, L. Fleming, J. Liu and O. Zhou., <u>Adv. Mater</u>., <u>14</u>, 235 (2002).

27. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, and R. E. Smalley, <u>Chem. Phys. Lett</u>., <u>313</u>, 91 (1999).

28. M. Lebron-Colon, <u>Thesis: Purification, Characterization and Functionalization of Single Wall Carbon Nanotubes for Aerospace Applications</u>, Chapter 2, 2005.

29. K. C. Chuang, D. A. Scheiman, J. Fu and M. Crawford, <u>J. Poly. Sci. A: Poly. Chem</u>., <u>37</u>, 2559 (1999).

30. J. Chen, M. A. Hannon, H. Hu, Y. Chen, A. M. Rao, P. Ecklund and R. C. Haddon, <u>Science</u>, <u>282</u>, 95 (1998).

31. J. E. Riggs, Z. Guo, D. L. Carroll and Y. P. Sun, <u>J. Am. Chem. Soc</u>., <u>122</u>, 5879 (2000).

32. P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave and R. E. Smalley, <u>Chem. Phys. Lett</u>., <u>310</u>, 367 (1999).

33. J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, <u>J. Am. Chem. Soc</u>., <u>123</u>, 6536 (2001).

34. J. L. Bahr, I. T. Mickelson, M. J. Bronikowski, R. E. Smalley and J. M. Tour, <u>Chem. Commun</u>., <u>2</u>, 193 (2001).

35. Y. Sun, S. R. Wilson and D. I. Schuster, <u>J. Am. Chem. Soc</u>., <u>123</u>, 5348 (2001).

36. V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger and A. Hirsch, <u>J. Am. Chem. Soc</u>., <u>124</u>, 760 (2002).

37. R. Bandyopadhyaya, E. Nativ-Roth, O. Regev and R.Yerushalmi-Rozen, <u>Nano Lett</u>., <u>2</u>, 25 (2002).