

Carbon Nanotubes and Nanofibre: An Overview

A. Chatterjee and B. L. Deopura*

Department of Textile Technology, IIT Delhi, New Delhi-110016, India
(Received July 12, 2002; Revised August 24, 2002; Accepted August 31, 2002)

Abstract: Carbon nanotubes are graphene sheets rolled up in cylinders with diameter as small as 1 nm. Extensive work carried out in recent years has revealed the intriguing properties of this novel material. Exceptional property combined with low density of nanotubes makes them suitable for use as reinforcements in composites. Low volume of production and high cost is the main limitations towards their growth and application. Nanofibres bridge the gap between the conventional carbon fibre and the carbon nanotubes. With their low cost & comparatively higher volume of production along with their exceptional properties, the nanofibres are considered attractive material as nanoscale reinforcement. In this article a concise review of structure, property, production and application of carbon nanotubes and nanofibres have been discussed.

Keywords: Carbon nanotube, Nanofibre, Production, Structure, Application

Introduction

In 1985 Smalley, Kroto and coworkers[1] discovered fullerene structure C_{60} (buckyball) and this led to the Noble Prize in chemistry in 1997. C_{60} is a soccer ball like molecule made of pure carbon atoms bonded in hexagon and pentagon configurations. The structure comprises of 60 carbon atoms arranged by 20 hexagonal and 12 pentagonal faces to form a sphere. The buckyball when elongated to form a long and narrow tube with a diameter of approximately 1 nm, it is called a nanotube. Iijima[2] in 1991 first discovered the quasi one-dimensional nanotube. The multi-walled carbon nanotubes (MWNTs) in carbon soot was made by an arc discharge method[2]. About two years later he reported single-walled nanotubes (SWNTs)[3]. Since then nanotubes have captured attention of researches worldwide. A lot of work has been done to understand the unique structural, electrical, mechanical, electromechanical and chemical properties of carbon nanotubes and the application of this novel material.

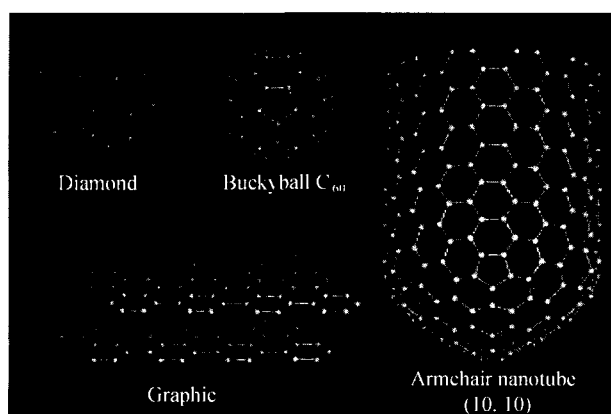


Figure 1. Different molecular structures of carbon based material [60].

In early 1960, Feynman[4] has predicted that the main focus of future science and technology would be on miniaturization, which will lead to designing of structure starting from the atomic scale. At that time this was of interests only to physicists and chemists.

The discovery of light and high strength nanotubes has revolutionized researches as an ideal structural member for designing nanostructural instrument and nanocomposite structure. Nanotubes have extraordinary mechanical, electrical and thermal properties.

The tensile modulus and strength of the nanotubes ranging from 270 GPa to 1 TPa and 11-200 GPa respectively have been reported[5,6]. Moreover, the nanotubes have high thermal and electrical conductivity far better than copper. In Figure 1 different crystal structures of carbon based material are shown.

Production of Nanotubes

The basic principle for the synthesis of carbon nanotubes is very simple: a carbonaceous feed stock has to be brought into gas phase where subsequently the evaporated species can self assemble into the tubular structures. The manufacturing processes of nanotubes include direct-current arc discharge [7-9], laser ablation[10], thermal and plasma enhanced chemical vapour growth deposition (CVD)[11,12] and self

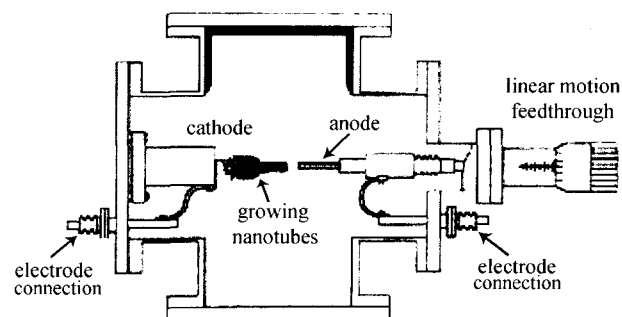


Figure 2. Schematic diagram of direct current arc discharge method.

*Corresponding author: bdeopura@textile.iitd.ernet.in

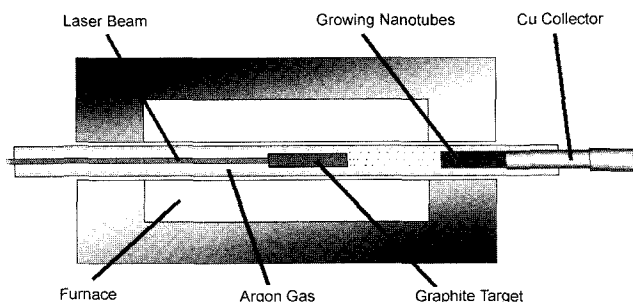


Figure 3. Schematic diagram of laser ablation method.

assembly of single crystals of SWNTs methods[13].

Historically, the electric arc discharge was the first technique for the production of both MWNTs[2] and SWNTs[3,14]. Using suitable catalysts and buffer gases, this technique was improved towards the growth of bundles of SWNTs in large amount[8]. Direct current arc discharge (Figure 2) and laser ablation (Figure 3) methods requires the addition of small amount of metal catalyst to increase the yield of the nanotubes. The products are normally tangled and in poorly ordered mat form. Although it was possible to make long individual nanotube with several hundred micron length, the difference in lattice arrangement in zigzag, armchair and chiral forms coexists in the products. In addition, these methods require very high temperature (arc discharge: 5000-20000 °C, laser ablation: 4000-5000 °C [15]), which make difficult the control of chirality and diameter of nanotubes. In a recent paper Maser *et al.*[16] has given a detail understanding of the nanotube production using concentrated light sources (laser/sunlight).

Both the arc discharge and laser ablation techniques are limited in the volume of samples they can produce in relation to the size of the carbon source (the anode in the arc discharge and target in the laser ablation). In addition subsequent purification steps are necessary to separate the tubes from undesirable by products. These limitations have motivated the development of gas phase techniques, such as chemical vapour deposition (CVD), where nanotubes are formed by the decomposition of a carbon containing gas [17]. The gas phase techniques can be used as a continuous process since the carbon source is continually replaced by flowing gas. Moreover, the purity of the nanotubes thus produced is quite high and requires less purification steps.

A number of techniques have been reported in literature for the production of carbon nanotubes using gas phase techniques[12,18-21] in which carbon monoxide or other hydrocarbon gas have been used as the source of carbon. Carbon monoxide based process gives high purity single-walled carbon nanotubes compared to hydrocarbon gas based process. The advantage of hydrocarbon gas based process is that it can operate at lower temperature of 600-700 °C and so a wide variety of substrates can be used for the growth of the nanotubes[17]. Although the low temperature dissociation of hydrocarbon affects the purity of the as processed nanotubes.

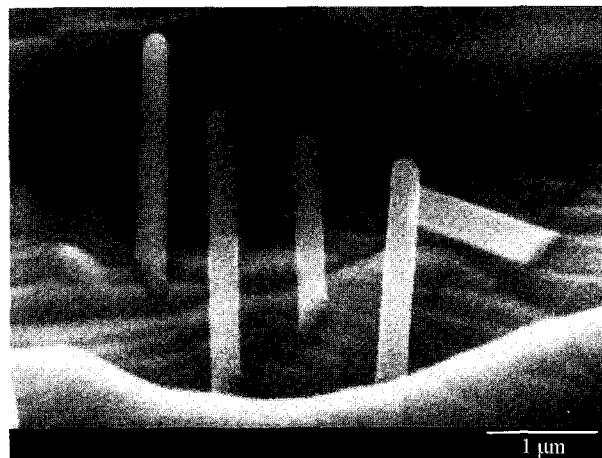


Figure 4. SWNTs on molybdenum substrate[13].

One unique aspect of CVD technique is its ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length. Plasma enhanced chemical vapour deposition has been successfully used for the synthesis of straight well aligned nanotubes, where the plasma is excited by a DC source[22-24] or a microwave source[25-29]. Figure 4 shows the SWNTs grown on molybdenum substrate.

Structure and Morphology of Carbon Nanotubes

Carbon nanotubes can be visualised as a sheet of graphite that has been rolled into a tube with end caps containing pentagonal rings. In general, the nanotubes can be specified in terms of tube diameter d , and the chiral angle θ . The chiral vector C_h is defined as a line connected from two crystallographically equivalent sites O and C on a two dimensional graphene structure. The chiral vector can be defined in terms of lattice translation indices (n, m) and the basic vector a_1 and a_2 of the hexagonal lattice[30], i.e.,

$$C_h = na_1 + ma_2. \quad (1)$$

Where the integers (n, m) are the number of steps along

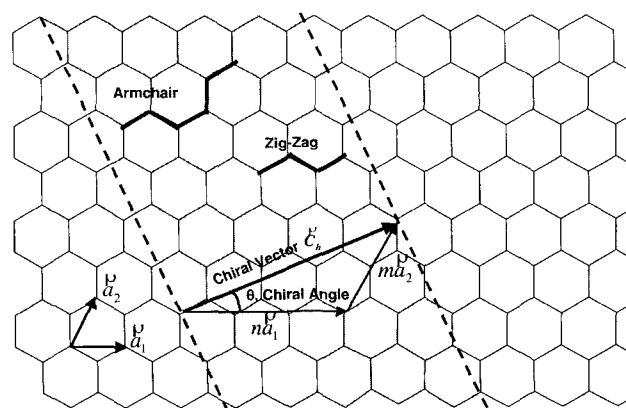


Figure 5. Schematic diagram of nanotube structure[17].

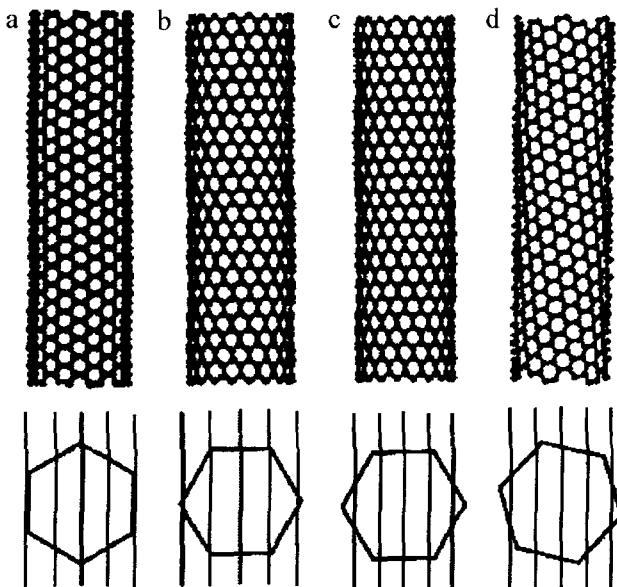


Figure 6. Schematic structures of SWNTs and how they determine the electronic properties. (a) A (10, 10) arm chair nanotube. Bottom panel: the hexagon represents the first Broulloin zone of a graphene sheet in reciprocal space. The vertical lines represent the electronic states of the nanotube. The centre line crosses two corners of hexagon, resulting in a metallic nanotube. (b) A (12, 0) zigzag nanotube. The electronic states cross the hexagon corners, but a small band gap can develop due to the curvature of the nanotube. (c) The (14, 0) zigzag tube is semiconducting because the states on the vertical lines miss the corner points of the hexagon. (d) A (7, 16) tube is semiconducting[31].

the zigzag carbon bonds of the hexagonal lattice and a_1 and a_2 are unit vectors (Figure 5)[17]. The chiral angle determines the amount of 'twist' in the tube. The two limiting cases are where the chiral angle is at 0° and 30° . These are zigzag and armchairs respectively based on the geometry of the carbon bonds around the circumference of the nanotube. In terms of the translational indices, the zigzag nanotube is $(n, 0)$ and the armchair nanotube is (n, n) . The electronic conductivity of nanotube is highly sensitive to a slight change of these parameters. Graphite is considered to be a semimetal, but it has been shown that nanotubes can either be metallic or semiconductor depending on chirality (Figure 6)[31].

Latest studies on electronic properties of nanotubes are focused on the tube-tube electrical transportability at different contact positions[32-34]. The resistance of contact region depends on the nanotube geometry and chirality. The conductance between nanotubes is higher when the two tubes are in registry and the contact region is commensurate. It has also been shown that the contact resistance depends on externally applied force or pressure.

Mechanical Property

Carbon nanotubes are acicular single crystals of high

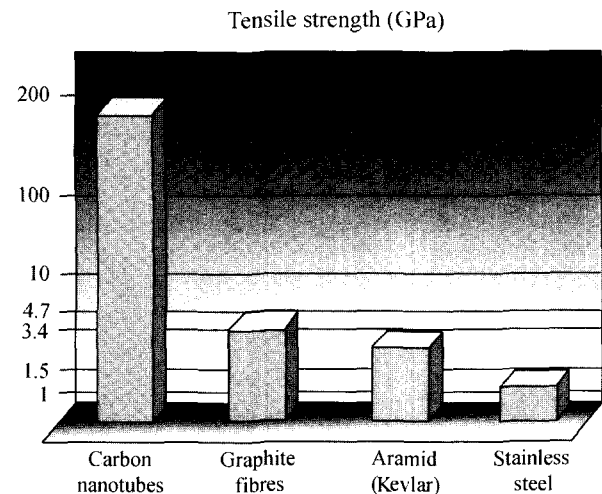


Figure 7. Comparison of the tensile strength of different engineering materials in log scale[60].

aspect ratio and having only few defects. It is chiefly this low density of defects that confers excellent mechanical properties to nanotubes. Moreover, the intrinsic strength of the Carbon-Carbon sp^2 bond is expected to give the carbon nanotubes the highest strength and modulus among all existing whiskers. In Figure 7, the comparison of the tensile strength of different engineering materials is shown.

The challenges in the characterisation of the nanotubes are (a) complete lack of micro mechanical characterisation techniques for direct property measurement, (b) tremendous limitations on specimen size, (c) uncertainty in data obtained from indirect measurements, and (d) inadequacy in test specimen preparation techniques[17].

In an earlier work, the elastic modulus of defect free nanotubes has been calculated by using the properties of graphite and was found to be approximately 1060 GPa[35]. Ruoff and Lorents[36] have estimated the tensile strength of nanotubes to be 20 GPa. Treacy *et al.*[37] estimated the elastic modulus of isolated multiwalled nanotubes by measuring the amplitude of their intrinsic thermal vibration. The average value reported was 1.8 TPa. Wong and coworkers [38] have studied the bending stiffness of cantilevered MWNTs by Atomic Force Microscopy (AFM). They found that the nanotubes were able to sustain a large elastic deformation without breakage, making them suitable for applications requiring storing or absorbing large amount of energy. According to Falvo *et al.*[39], nanotubes can sustain repeated bending as high as a local strain of 16% without failure. Rochefort *et al.*[40] have studied computationally the bending and twisting of nanotubes. They found that the electrical resistance of nanotubes increases with increasing bending angle. It is also being reported[41] that the bending modulus of nanotubes decreases rapidly with increasing diameter of the nanotube due to formation of wave like distortion on the surface of the nanotubes. Ru[42,43] have used a continuum multi-shell elastic model to study the buckling behaviour of nanotubes under uniaxial compressive

load. He concluded that the nanotubes were remarkably resilient. It can sustain large strain without any sign of brittleness, plasticity or atomic rearrangement. Yu *et al.*[44] have investigated the tensile loading of MWNTs using AFM. The failure of the outermost tube occurred followed by pullout of the inner nanotubes. The experimentally calculated tensile strength of the outermost layer ranged from 11 to 63 GPa and the elastic modulus ranged from 270 to 950 GPa.

The SWNTs tend to assemble in ropes of nanotubes. Silvetat *et al.*[45] measured the properties of these nanotube bundles with AFM. As the diameter of the tube bundles increases, the axial and the shear moduli decrease significantly. This suggests slipping of nanotubes within the bundle. The elastic strain of nanotube bundles was investigated by Walters *et al.*[46] using AFM. They calculated yield strength of 45 ± 7 GPa for the nanotube ropes.

Srivastava *et al.*[47] have reported a new mechanism for the collapse and plasticity of compressed thin nanotubes. The relaxation of the strain energy in the collapsed section of the tube causes immediate graphitic to diamond-like bonding reconstruction at the location of the collapse. In all simulations, carbon nanotubes, when subjected to large deformations, switch into different shapes accompanied by abrupt release of stress energy[48]. The bending is fully reversible up to very large bending angles despite the occurrence of kinks and highly strained tubule regions. This is due to the ability of the sp^2 network C-C bonds to reversibly change hybridization when deformed out of plane.

Carbon Nanofibre

Carbon nanofibre are a unique form of vapour-grown carbon fibre that bridge the gap between the larger, conventional PAN or pitch based carbon fibres and the smaller single-wall or multi-wall carbon nanotubes. The nanofibres have transport and mechanical properties that approach the theoretical values of single crystal graphite, similar to the nanotubes, but can be produced in high volume at low cost. Investigations performed over last thirty



Figure 8. SEM image of as grown Pyrograf™-III carbon nanofibres (Courtesy: Pyrograf Products, Inc. USA).

Table 1. Properties of vapour grown carbon nanofibre*

Property	As grown	Heat treated
Tensile Strength (GPa)	2.7	7.0
Modulus (GPa)	400	600
Ultimate strain (%)	1.5	0.5
Density (g/cc)	1.8	2.1
Electrical resistivity ($\mu\text{ohm-cm}$)	1000	55
Thermal conductivity (W/m-K)	20	1950

*Courtesy: Pyrograf Products Inc. USA

years mainly devoted to the understanding the growth mechanism and property development from various similar gas phase techniques[49-51]. Figure 8 shows the typical SEM image of as grown carbon nanofibres. Some typical properties of carbon nanofibres are given in Table 1.

Nanofibre Morphology

Vapour phase produced carbon nanofibres are similar to fullerene nanotubes in the nanoscale domain of initial formation and highly graphitic structure of the initial filament. Carbon nanofibres are made by a variation of the vapour-phase catalytic method in which a carbon containing feedstock is pyrolysed in the presence of small metal catalyst particles[52-54]. The nanofibre growth normally proceeds in a two-stage process of lengthening followed by thickening[49,53,55]. In the first stage, carbon from the hot atmosphere is absorbed into the catalyst particle and then precipitates out on one side to form a highly graphitic strand with a diameter roughly equal to that of the catalyst particle. After lengthening, chemical vapour deposition of carbon covers the catalyst and builds up the diameter of the nanofibre.

Application

It is rightly said that if good things come in small packages, then the tiniest package should harbor the best things, such is the thinking surrounding carbon nanotubes. The tubular structure of nanotubes imparts exceptional mechanical and electronic properties to the carbon nanotubes. The short list of attributes includes super strength, combined with low weight, stability, flexibility, good heat conductance, large surface area and a host of intriguing electronic properties.

The experimental activity in the nanotube/fibre field is currently very large and broad. A few examples include observations of metallic transport and nonlinear on-tube devices including rectifier[56] and transistor[57], single electron transport[58] and behaviour suggesting 1D electronic structure[59]. Other applications include the possibilities associated with the strength of nanotubes/fibres. It is well understood that carbon nanotubes/fibres can not be used alone without any supporting medium or matrix to form structural components. As a consequence, there has been

recent interest in the development of nanotube/fibre based composites. Although most of the work is focused on the development of polymer based composites, attempts have also been made to develop metal and ceramic matrix composites.

Conclusion

Carbon nanotubes and nanofibres have exceptional properties and have tremendous potential as material for nanoscale reinforcement. Extensive research going on worldwide will definitely led to development of composites having superior properties.

References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
2. S. Iijima, *Nature*, **354**, 56 (1991).
3. S. Iijima and T. Ichihashi, *Nature*, **363**, 603 (1993).
4. R. P. Feynman, *J. Microelectromech. Syst.*, **1**, 60 (1992).
5. J. P. Lu, *J. Phys. Chem. Solids*, **58**, 1649 (1997).
6. F. Li, B. S. Cheng, and G. Su, *Appl. Phys. Lett.*, **77**, 3161 (2000).
7. C. Journet and P. Bernier, *Appl. Phys. A*, **67**, 1 (1998).
8. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. de la Chapelle, A. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, *Nature*, **388**, 756 (1997).
9. B. I. Yakobson and R. E. Smalley, *Am Scient*, **85**(4) (1997).
10. A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. RodriguezMacias, P. J. Boul, A. H. Lu, D. Heymann, D. T. Colbert, R. S. Lee, J. E. Fischer, A. M. Rao, P. C. Eklund, and R. E. Smalley, *Appl. Phys. A*, **67**, 29 (1998).
11. M. Endo, K. Takeuchi, K. Kobori, K. Takahashi, H. W. Kroto, and A. Sarkar, *Carbon*, **33**, 873 (1995).
12. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Fohm-und, D. T. Colbert, K. A. Smith, and R. E. Smalley, *Chem. Phys. Lett.*, **313**, 91 (1999).
13. R. R. Schlittler, J. W. Seo, J. K. Gimzewski, C. Durkan, M. S. M. Saifullah, and M. E. Welland, *Science*, **292**, 1136 (2001).
14. D. S. Belhune, C. H. Kiang, M. S. DeVries, G. Gorman, R. Savoy, and R. Beyers, *Nature*, **363**, 605 (1993).
15. L. C. Qin, D. Zhou, A. R. Krauss, and D. M. Gruen, *Appl. Phys. Lett.*, **72**, 3399 (1998).
16. W. K. Maser, A. M. Benito, and M. T. Martinez, *Carbon*, Article in press (2002).
17. E. T. Thostenson, Z. Ren, and T. W. Chou, *Composites Science and Technology*, **61**, 1899 (2001).
18. M. Ge and K. Sattler, *Appl. Phys. Lett.*, **64**(6), 710 (1994).
19. G. Che, B. B. Lakshmi, C. R. Martin, E. R. Fisher, and R. S. Rouff, *Chem. Mater.*, **10**(1), 260 (1998).
20. W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, and W. Y. Zho, *Science*, **274**, 1701 (1996).
21. X. X. Zhang, Z. Q. Li, G. H. Wen, K. K. Fung, J. Chen, and Y. Li, *Chem. Phys. Lett.*, **333**(6), 509 (2001).
22. Z. F. Ren, Z. P. Huang, J. W. Xu, and J. H. Wang, *Appl. Phys. Lett.*, **75**(8), 1086 (1999).
23. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, and M. P. Siegal, *Science*, **282**, 1105 (1998).
24. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, M. P. Siegal, and P. N. Provencio, *Appl. Phys. Lett.*, **73**(26), 3845 (1998).
25. C. Bower, W. Zhu, S. Jin, and O. Zhou, *Appl. Phys. Lett.*, **77**(6), 830 (2000).
26. C. Bower, O. Zhou, W. Zhu, D. J. Werder, and S. Jin, *Appl. Phys. Lett.*, **77**(17), 2767 (2000).
27. H. Cui, O. Zhou, and B. R. Stoner, *J. Appl. Phys.*, **88**(10), 6072 (2000).
28. M. Okai, T. Muneyoshi, T. Yaguchi, and S. Sasaki, *Appl. Phys. Lett.*, **77**(21), 3468 (2000).
29. Y. C. Choi, Y. M. Shin, Y. H. Lee, B. S. Lee, G. S. Park, and W. B. Choi, *Appl. Phys. Lett.*, **76**(17), 2367 (2000).
30. M. S. Dresselhaus, G. Dresselhaus, and R. Satio, *Phys. Rev. B*, **45**, 6234 (1992).
31. H. Dai, *Surface Science*, **500**, 218 (2002).
32. S. Paulson, A. Helser, M. B. Nardelli, R. M. Taylor II, and M. Falvo, *Science*, **290**, 1742 (2000).
33. M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, and P. L. Mceuen, *Science*, **288**, 494 (2000).
34. A. Buldum and J. P. Lu, *Phys. Rev. B*, **63**16, 1403 (2001).
35. B. T. Kelly in "Physics of Graphite", Appl. Sci., London, 1981.
36. R. S. Ruoff and D. C. Lorents, *Carbon*, **33**, 925 (1995).
37. M. M. J. Treacy, T. W. Ebbesen, and T. M. Gibson, *Nature*, **381**, 680 (1996).
38. E. C. Wong, P. E. Sheehan, and C. M. Lieber, *Science*, **277**, 1971 (1997).
39. M. R. Falvo, G. J. Clary, R. M. Taylor, V. Chi, F. P. Brook, and S. Washburn, *Nature*, **389**, 582 (1997).
40. A. Rochefort, P. Avouris, F. Lesage, and D. R. Salahub, *Phys. Rev. B*, **60**, 13824 (1999).
41. P. Poncharal, Z. L. Wang, D. Ugrate, and W. Heer, *Science*, **283**, 1513 (1999).
42. C. Q. Ru, *Phys. Rev. B*, **62**, 9973 (2000).
43. C. Q. Ru, *J. Appl. Phys.*, **89**, 3426 (2001).
44. M. F. Yu, O. Lourie, M. Dyer, K. Moloni, and T. Kelly, *Science*, **287**, 637 (2000).
45. J. P. Salvetat, G. A. D. Briggs, J. M. Bonard, R. R. Bacsá, and A. J. Kulik, *Phys. Rev. Lett.*, **82**(5), 944 (1999).
46. D. A. Walters, L. M. Ericson, M. J. Casavant, J. Liu, D. T. Colbert, and K. A. Smith, *Appl. Phys. Lett.*, **74**(25), 3803 (1999).
47. D. Srivastava, M. Menon, and C. Kyeongjae, *Phys. Rev. Lett.*, **83**(15), 2973 (1999).
48. M. Buongiorno Nardelli, B. I. Yakobson, and J. Bernholc,

- Phys. Rev. B*, **57**(8), R4277 (1998).
49. N. M. Rodriguez, *J. Mater. Res.*, **8**, 3233 (1993).
50. C. H. Bartholomew, *Catal. Rev. Sci. Eng.*, **24**, 67 (1982).
51. D. L. Trim, *Catal. Rev. Sci. Eng.*, **16**, 155 (1977).
52. A. Oberlin, M. Endo, and T. Koyama, *J. Cryst. Growth*, **32**, 335 (1976).
53. R. T. K. Baker, *Carbon*, **27**(3), 315 (1989).
54. G. G. Tibbetts, *J. Cryst. Growth*, **66**, 632 (1984).
55. G. G. Tibbetts, *Carbon*, **30**, 399 (1992).
56. P. G. Collins, A. Zettl, H. Bando, A. Thess, and R. E. Smalley, *Science*, **278**, 100 (1997).
57. P. L. McEuen, *Nature*, **393**, 15 (1998).
58. M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, and R. E. Smalley, *Science*, **275**, 1922 (1997).
59. S. J. Tans, M. H. Devoret, R. J. A. Groeneveld, and C. Dekker, *Nature*, **394**, 761 (1998).
60. A. K. Lau and D. Hui, *Composites B*, **33**, 267 (2002).