

Covalent crosslinking of carbon nanostructures

URMIMALA MAITRA, M PANDEESWAR and T GOVINDARAJU*

New Chemistry Unit, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India
e-mail: tgraju@jncasr.ac.in

MS received 29 September 2011; revised 16 December 2011; accepted 30 December 2011

Abstract. Covalent crosslinking of carbon nanostructures of different dimensionalities such as nanodiamond, single walled carbon nanotubes (SWNTs) and graphene can yield useful homo- and hetero-binary conjugates. Binary conjugation of the nanocarbons has been achieved by introducing symmetrical amide-linkages between acid (-COOH) functionalized nanocarbons and a diamine-linker. The binary conjugates have been characterized by using transmission electron microscopy as well as infrared, Raman and photoluminescence spectroscopies. Dispersions of covalently crosslinked binary conjugates of nanocarbons could be obtained in dimethyl formamide (DMF). Composites of the binary conjugates with polymer can be readily prepared by using the DMF suspensions.

Keywords. Covalent crosslinking; carbon nanostructures; binary conjugates; nanocomposites; electron microscopy; optical properties.

1. Introduction

One of the important factors that determines the nature and properties of nanomaterials is their dimensionality. Among the various nanomaterials synthesized and characterized in recent years, nanocarbons of different dimensionalities are of special interest. In the nanocarbon family, we have zero-dimensional nanodiamond, one-dimensional carbon nanotubes and two-dimensional graphene. There has been a vast amount of research on the properties of the individual nanocarbons. Nanodiamond (ND) exhibits useful mechanical, electrical and optical properties.^{1–6} Beneficial properties of single walled carbon nanotube (SWNTs) are well-documented,^{7–9} while those of graphene (G) have been discovered more recently.¹⁰ Binary combinations of nanocarbons with different dimensionalities may lead to integration of properties of the constituents units as well as result in new properties. It could be of some advantage if binary combinations of nanostructures are prepared by covalent modification over non-covalent methods. Covalently linked carbon nanostructures in particular, hetero-combinations will have better interactions among the two nanostructures which are easy to understand and may lead to improved properties. One of the effects of a component nanostructure in the conjugate may synergistically benefit the mechanical properties of the hetero-binary conjugate because of better mixing

which facilitates greater interactions among the individual components. It has been found recently that extraordinary synergy in mechanical properties resulted from incorporating two nanocarbons into polymer matrices.¹¹ In this case the binary combination was achieved by just physical mixing. Covalently linked nanocarbons could provide better insight into the mechanism of origin of such synergistic effects reflected in the mechanical properties. Again ND-SWNT composites have been used to prepare cold cathodes.¹² Covalently linked ND with SWNT can be studied for enhanced activities in such applications as well. In general, covalent conjugates of carbon nanostructures, in particular hetero-binary conjugates are fundamentally important in understanding the synergistic effect observed in the derived composites and may find applications as high performance materials. There are only few reports on the covalent crosslinking of carbon nanotubes. Chiu *et al.*¹³ have reported crosslinking of two chloride terminated carbon nanotubes via diamines while Frehill *et al.*¹⁴ have used inorganic metal complexes to crosslink carbon nanotubes. Bundles of carbon nanotubes can be linked by means of [2+1] cycloaddition using nitrenes.¹⁵ To our knowledge, there are no reports on the covalent conjugation of nanocarbons of different dimensionalities. We have therefore carried out covalent crosslinking of carbon nanostructures with similar or different dimensionalities. Besides the preparation of crosslinked NDs, SWNTs and G, we have synthesized different hetero-nanocarbon combinations such as

*For correspondence

ND + SWNT, ND + G and G + SWNT. Such homo- and hetero-nanocarbon adducts may find use in special applications related to high performance materials.

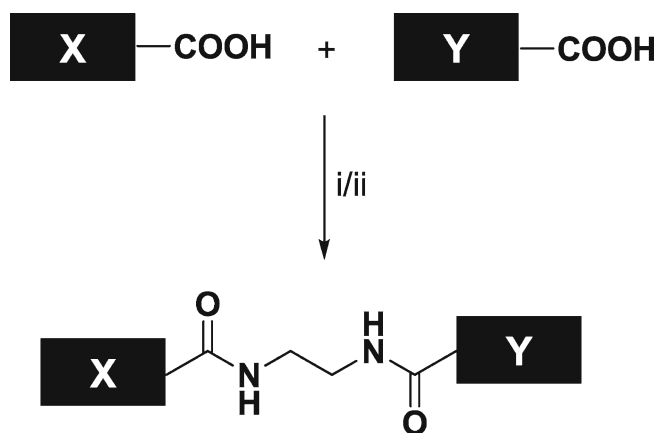
2. Experimental

Nanodiamond (ND) with phase purity higher than 98% and an average particle size of around 5 nm was purchased from Tokyo Diamond Tools, Tokyo, Japan. Few-layer graphene (G) was prepared by the exfoliation of graphite oxide following the procedure described recently.¹⁶ Single walled carbon nanotubes (SWNTs) prepared by the DC arc-discharge process were treated with dilute HCl and heated under hydrogen atmosphere several times to remove the metal nanoparticles and amorphous carbon.¹⁷ Mono protected *N*1-(*t*-Boc)-1,2-ethylenediamine was synthesized following the modified procedure reported in the literature (Supporting Information).¹⁸

In order to prepare binary homoconjugates of ND, G and SWNT, each of these carbon nanostructures was treated to create surface carboxyl groups. A diamine linker was then used to covalently conjugate the acid functionalized nanocarbons. *N,N'*-Dicyclohexylcarbodiimide (DCC) was used as the coupling reagent to enhance the reaction of acid functionalized nanocarbons with the diamine. In a typical experiment with ND, 100 mg of the nanocarbon was refluxed with conc. HNO₃ (5 mL) and conc. H₂SO₄ (45 mL) for 12 h. The acid-functionalized nanodiamond (ND-COOH) was washed with distilled water and dried under vacuum.¹⁹ SWNTs and G were functionalized with acid groups by heating a mixture of nanocarbon with conc. HNO₃, conc. H₂SO₄ and water in a microwave oven for about 5–8 min under hydrothermal conditions, followed by further heating at 100°C for 6–8 h in an oven. The product thus obtained was washed with distilled water and filtered through a sintered glass funnel to yield acid functionalized nanocarbons SWNT-COOH and G-COOH.^{7,19–22}

To prepare binary nanocarbon homoconjugates, the acid-functionalized nanocarbon (5 mg) of interest was taken in DMF (20 mL), sonicated for 10 min for thorough mixing. To this mixture, coupling reagent DCC (1 mg) and 1,2-ethylenediamine (ED) (1 mL) were added. Reaction mixture was stirred for 4 h under inert atmosphere and the products were collected by centrifugation. The product was washed with copious amounts of water, acetonitrile and ethanol. The sample was dried *in vacuo* and used for further characterization. For the preparation of binary heteroconjugates of nanocarbons, a two-step covalent crosslinking procedure was followed. Mono-protected Boc-1,2-ethylenediamine was first

coupled to an acid functionalized nanocarbon through an amide linkage which was then subjected to boc-deprotection using trifluoroacetic acid. The nanocarbon with the free amine was coupled to another acid functionalized nanocarbon through an amide linkage to obtain the ED linked binary heteroconjugate. This procedure eliminates the possibility of obtaining undesired products resulting from inter- and intramolecular cross-coupling reactions. In a typical reaction an acid functionalized nanocarbon (5 mg) was taken in DMF (20 mL), sonicated for 10 min to get a homogenous mixture. To this mixture DCC (1 mg) and mono-protected boc-1,2-ethylenediamine (1 mL) were added. The reaction mixture was stirred for 4 h under inert atmosphere and the products were collected by centrifugation. The product was washed with copious amounts of water, acetonitrile and ethanol, dried *in vacuo*. The mono boc-1,2-ethylenediamine modified nanocarbon was subjected to boc-deprotection using 50% trifluoroacetic acid in dichloromethane for 1 h. The ED-nanocarbon containing free amine was dried *in vacuo* and used for further reaction. The ED functionalized nanocarbon (5 mg) and an acid functionalized nanocarbon (5 mg) were dispersed in DMF (20 mL) and sonicated for 10 min for thorough mixing. To this mixture DCC (1 mg) was added and reaction was stirred for 4 h under inert atmosphere and the conjugate was collected by centrifugation. The product was washed with water, acetonitrile and ethanol, dried *in vacuo* and used for characterization.



Scheme 1. Preparation of binary conjugates. Nanocarbons (X, Y): ND, SWNT and G containing COOH groups. (i) For homoconjugates: nanocarbon (X = Y), DCC, ED, DMF, 4 h. (ii) For heteroconjugates: (a) nanocarbon (X), mono-boc-ethylenediamine, DCC, DMF, 4 h followed by TFA-DCM (1:1), 1 h. and (b) nanocarbon (Y, Y ≠ X), DCC, DMF, 4 h. Homo- and hetero-conjugates prepared: ND-ND (1), G-G (2), SWNT-SWNT (3), ND-G (4), G-SWNT (5) and ND-SWNT (6).

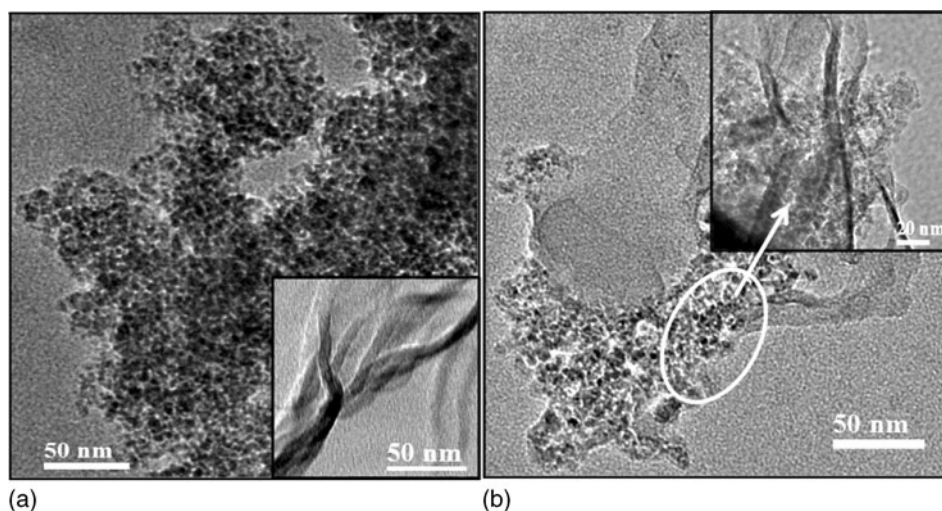


Figure 1. TEM images of (a) ND-ND conjugate and a G-G conjugate (in the inset) and (b) of a ND-G conjugate (with magnified version in the inset).

The homo- and hetero-conjugates of nanocarbons were characterized using spectroscopic and microscopic techniques. Transmission electron microscope (TEM) micrographs were obtained with a JEOL JEM 3010, operating with an accelerating voltage of 300 kV. Infrared (IR) spectra were recorded on Bruker IFS 66v/S spectrometer. Raman spectra were recorded with a LabRAM HR high-resolution Raman spectrometer (Horiba-Jobin Yvon) using a He-Ne laser ($\lambda = 632.8$). Photoluminescence (PL) spectra were recorded with a Perkin-Elmer model LS55 luminescence spectrometer.

3. Results and discussion

Homo- and hetero-conjugates of ND, SWNT and G were prepared as described in scheme 1 by using 1,2-

ethylenediamine linker to selectively conjugate two same or different nanocarbons. Nanocarbons of same type were covalently linked through amide linkages to obtain symmetrical homoconjugates in a one-step process, whereas a two-step amide linkage process was followed to obtain heteroconjugates containing two nanocarbons of different dimensionalities. Figure 1a shows the TEM micrographs of ND-ND (1) with G-G (2) homoconjugates. ND exists in the form of small clusters and these clusters crosslink to each other as a result of covalent conjugation forming larger clusters. Similarly, graphene sheets crosslink to each other mostly through the edges. In case of ND-G, clusters of ND are covalently crosslinked to G sheets as shown in the image in figure 1b. Figures 2a and b show the TEM images of G-SWNT and ND-SWNT heteroconjugates,

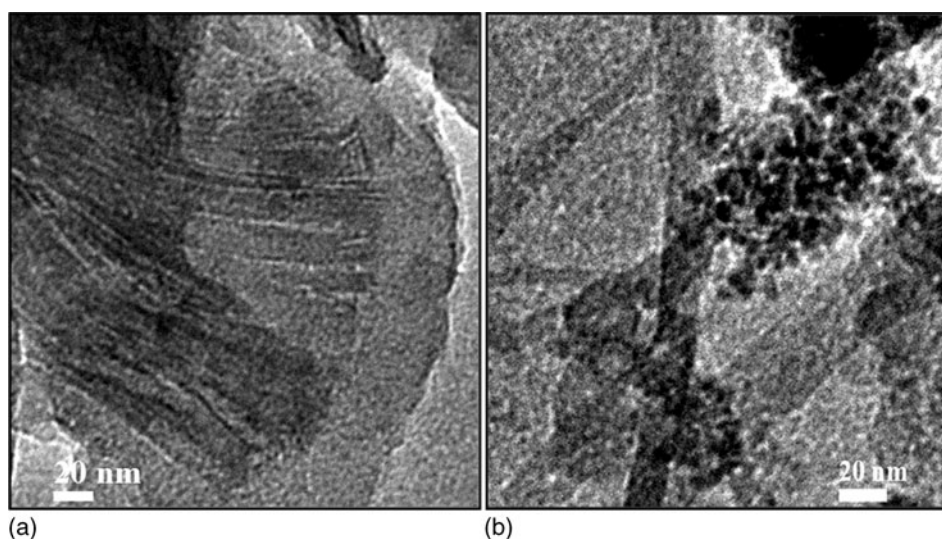


Figure 2. TEM image of (a) G-SWNT conjugate and (b) ND-SWNT conjugate.

respectively. The association of two nanocarbons could be observed uniformly throughout the sample due to the crosslinking of the SWNT bundles with G sheets and with the ND clusters. Definitive evidence for covalent crosslinking between nanocarbons to form homo- or hetero-conjugates is provided by spectroscopic studies. Thus, infrared spectroscopy clearly shows characteristic bands arising from conjugating as can be seen from typical spectra shown in figure 3, in the case of homo- and hetero-conjugates formed by graphene.

We see the presence of amide bands in the spectra of conjugates besides C-H stretching band arising from the linker. In the covalent binary conjugates the C=O peak shifted to lower frequencies (1715 cm^{-1}) than that of corresponding acids (1730 cm^{-1}).

Raman spectroscopy also provides evidence for crosslinking especially in the case of heteroconjugates. We have shown Raman spectra of the conjugates formed by graphene and to illustrate this aspect. We see that G-ND shows the 2D band ($\sim 2600\text{ cm}^{-1}$) characteristic of the few-layer graphene,²³ the band being absent in the spectrum of ND (figure 4). The Raman spectrum of SWNT-G shows characteristic bands due to the

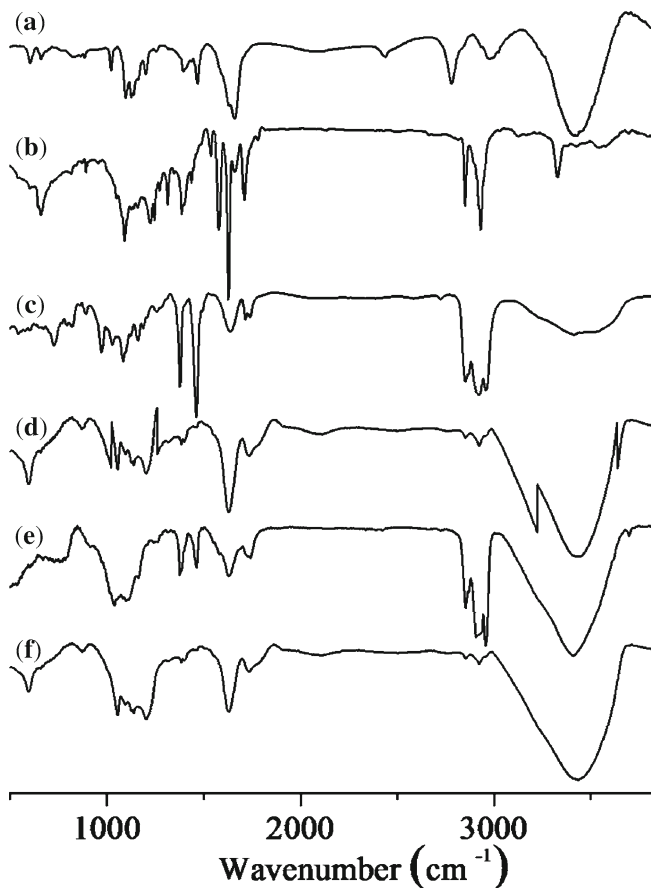


Figure 3. IR spectra of (a) ND-SWNT, (b) ND-G, (c) ND-ND, (d) SWNT-COOH, (e) G-COOH and (f) ND-COOH.

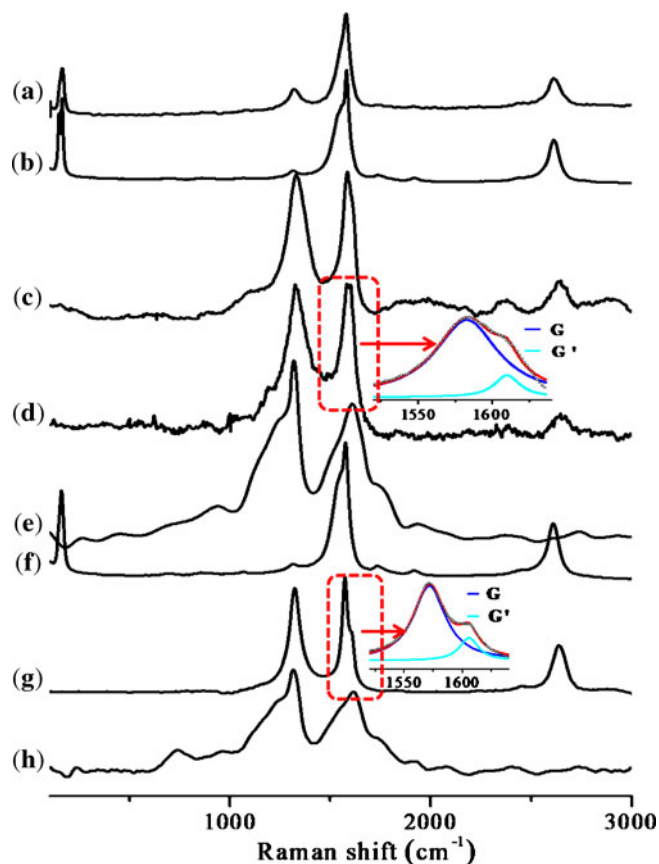


Figure 4. Raman spectra of (a) G-SWNT, (b) ND-SWNT, (c) ND-G, (d) G-G, (e) ND-ND, (f) SWNT-COOH, (g) G-COOH and (h) ND-COOH.

radial breathing mode (RBM) of the SWNTs (~ 140 and 160 cm^{-1}).²⁴ These bands are also seen in the spectrum of SWNT-ND. The ratio of the intensities of the 2D and

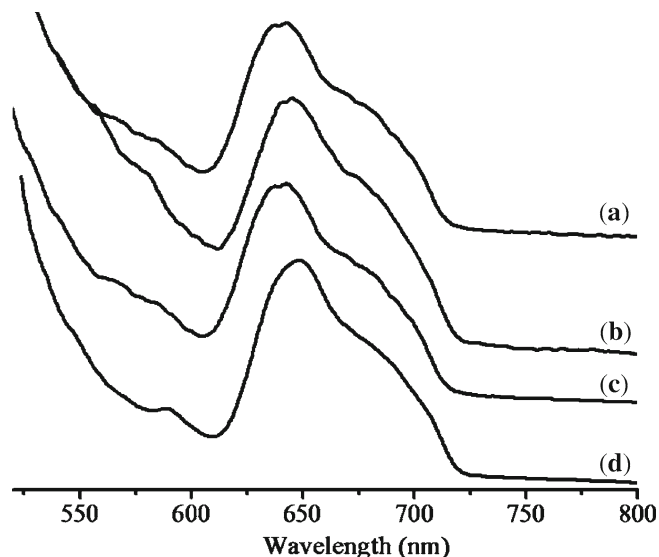


Figure 5. Photoluminescence spectra of (a) ND-SWNT, (b) ND-G, (c) ND-ND and (d) ND-COOH.

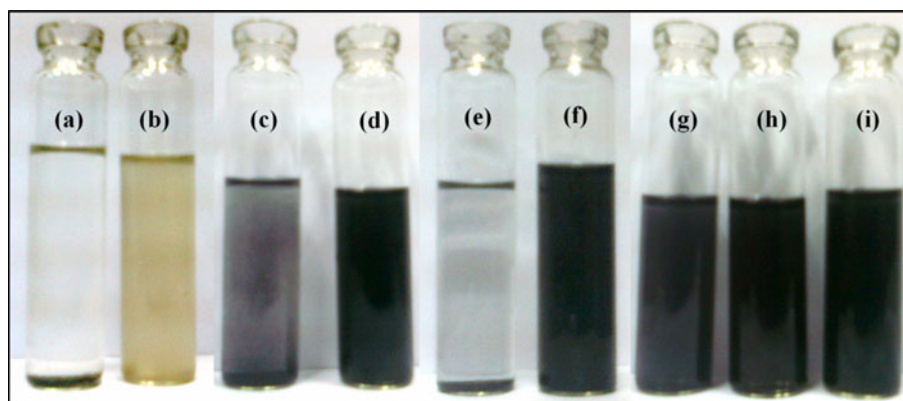


Figure 6. Photographs of dispersions of (a) ND-COOH, (b) ND-ND, (c) G-COOH, (d) G-G, (e) SWNT-COOH, (f) SWNT-SWNT, (g) ND-SWNT, (h) ND-G and (i) G-SWNT in DMF.

G Raman bands, I_{2D}/I_G in graphene conjugate is smaller than in the graphene showing the effect of crosslinking of the electronic structure of graphene. It may be noted that the I_{2D}/I_G ratio is very sensitive to doping and with electron donating and withdrawing molecules reduce the I_{2D}/I_G ratio of graphene.²⁵

The photoluminescence spectrum of ND (~650 nm) is seen in all the conjugates containing ND (figure 5). The photoluminescence bands of the binary composites show a red shift as compared to that of ND-COOH. The observed photoluminescence in case of ND and ND containing binary conjugates originates from the nitrogen and vacancies (NV centres) as reported in the literature.^{26,27} Though we have not understood the actual reason for red-shift observed in the photoluminescence of ND containing binary conjugates, it is a clear evidence of synergistic effect transferred from individual carbon nanostructures to their binary conjugates.

Interestingly, all the covalently crosslinked binary conjugates of nanocarbons form stable homogenous dispersions in dimethyl formamide. In figure 6 we show the photographs of dispersion of acid treated nanocarbons and their conjugates in DMF. Acid treated nanocarbons do not disperse well in DMF while all the homo- and hetero-binary conjugates disperse and at least for 6 h at a concentration of 1 mg/3 mL. This better dispersibility of the binary conjugates can be due to the presence of unused amine groups left on the surface of nanocarbons in binary conjugates.

The dispersions of nanocarbon conjugates can be used for the preparation of polymer-nanofiller composites by using polymers that dissolve in DMF. Thus, we were able to prepare homogenous films of polyethylene oxide (PEO, molecular weight 20,000 g) containing binary nanocarbon composite fillers. Mechanical properties of homo- and hetero-binary conjugates of carbon nanostructures and their polymer composites can be

studied to explore the applications related to high performance materials.

4. Conclusions

In conclusion, we have successfully prepared covalent homo- and hetero-binary conjugates of nanodiamond, SWNT and graphene, by using a diamine as the crosslinking agent. This procedure is convenient and effective for conjugation of two nanocarbon moieties through amide linkages. The binary conjugates of nanocarbons form stable dispersions in dimethyl formamide. These dispersions of nanocarbon binary conjugates can be used to prepare composites with polymers. The homo- and hetero-binary conjugates of carbon nanostructures and their polymer composites may find applications related to high performance materials.

Supporting information

Supporting information figure S1 (Raman spectral data), figures S2–S3 (NMR and mass data), table S1 (Raman spectral data), can be seen in www.ias.ac.in/chemsci.

Acknowledgements

Authors thank Prof. C N R Rao, Jawaharlal Nehru Centre for Advanced Scientific Research for constant support and encouragement.

References

1. D'Evelyn M P 1998 Surface Properties of diamond. In *Handbook of industrial diamonds and diamond films* (eds.) M A Prelas, G Popovici and L K Bigelow (New York: Marcel Dekker Inc.) p 89

2. Dolmatov V Y 2001 *Russ. Chem. Rev.* **70** 607
3. Zhu W, Kochanski G P and Jin S 1998 *Science* **282** 1471
4. Yu S J, Kang M W, Chang H C, Chen K M and Yu Y C 2005 *J. Am. Chem. Soc.* **127** 17604
5. Fu C C, Lee H Y, Chen K, Lim T S, Wu H Y, Lin P K, Wei P K, Tsao P H, Chang H C and Fann W 2007 *Proc. Natl. Acad. Sci. USA* **104** 727
6. Zhao W, Qiu J X Q and Chen H Y 2006 *Biosens. Bioelectron.* **22** 649
7. Rao C N R and Govindaraj A 2005 *Nanotubes and Nanowires*; Royal Society of Chemistry: Cambridge, UK
8. Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes*, Imperial College Press: London, UK
9. (a) Dai H 2002 *Acc. Chem. Res.* **35** 1035; (b) Banerjee S, Hemraj-Benny T and Wong S-S 2005 *Adv. Mater.* **17** 17
10. Rao C N R, Sood A K, Subrahmanyam K S and Govindaraj A 2009 *Angew. Chem. Int. Ed.* **48** 7752
11. Prasad K E, Das B, Maitra U, Ramamurty U and Rao C N R 2009 *Proc. Natl. Acad. Sci. USA* **106** 13186
12. Guglielmotti V, Chieppa S, Orlanducci S, Tamburri E, Toschi F, Terranova M L and Rossi M 2009 *Appl. Phys. Lett.* **95** 222113
13. Chiu P W, Duesburg G S, Weglikowska U D and Roth S 2002 *Appl. Phys. Lett.* **80** 3811
14. Frehill F, Vos J G, Benrezzak S, Koós A A, Kónya Z, Rütther M G, Blau W J, Fonseca A, Nagy J B, Biró L P, Minett A I and Panhuis M 2002 *J. Am. Chem. Soc.* **124** 13694
15. Holzinger M, Steinmetz J, Samaille D, Glerup M, Paillet M, Bernier P, Ley L and Graupner R 2004 *Carbon* **42** 941
16. Avinash M B, Subrahmanyam K S, Sundarayya Y and Govindaraju T 2010 *Nanoscale* **2** 1762
17. Dresselhaus M S, Jorio A and Saito R 2010 *Annu. Rev. Condens. Matter Phys.* **1** 89
18. Dresselhaus M S and Eklund P C 2000 *Adv. Phys.* **49** 705
19. Das B, Voggu R, Rout C S and Rao C N R 2008 *Chem. Commun.* **41** 5155
20. Weglikowska U D, Benoit J M, Chiu P W, Graupner R, Lebedkin S and Roth S 2002 *Curr. Appl. Phys.* **2** 497
21. Rao C N R, Biswas K, Subrahmanyam K S and Govindaraj A 2009 *J. Mater. Chem.* **19** 2457
22. Jaramillo D, Wheate N J, Ralph S F, Howard W A, Tor Y, Aldrich-Wright J R 2006 *Inorg. Chem.* **45** 6004
23. Maitra U, Gomathi A and Rao C N R 2008 *J. Exp. Nanosci.* **3** 271
24. Subrahmanyam K S, Ghosh A, Gomathi A, Govindaraj A and Rao C N R 2009 *Nanosci. Nanotech. Lett.* **1** 28
25. Rao C N R, Sood A K, Voggu R, Subrahmanyam K S 2010 *J. Phys. Chem. Lett.* **1** 572
26. Chung P-H, Perevedentseva E and Cheng C-L 2007 *Surf. Sci.* **601** 3866
27. Vlasov I I, Shenderova O, Turner S, Lebedev O I, Basov A A, Sildos I, Rähn M, Shiryaev A A and Tendeloo G V 2010 *Small* **6** 687