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Single step process for the synthesis of carbon nanotubes and metal/alloy-filled multiwalled carbon nanotubes

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Abstract A single-step approach for the synthesis of multi-walled nanotubes (MWNT) filled with nanowires of Ni/ternary Zr based hydrogen storage alloy has been illustrated. We also demonstrate the generation of CO-free hydrogen by methane decomposition over alloy hydride catalyst. The present work also highlights the formation of single-walled nanotubes (SWNT) and MWNTs at varying process conditions. These carbon nanostructures have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), Energy dispersive X-ray analysis (EDX) and Raman spectroscopy. This new approach overcomes the existing multi-step process limitation, with possible impact on the development of future fuel cell, nano-battery and hydrogen sensor technologies.

Keywords Carbon nanotubes · Nanowires · Encapsulation · Hydrogen production · Alloys · Chemical vapour deposition

Filling carbon nanotubes (CNTs) has prompted significant progress in preparation of novel materials with potential control over their intrinsic mechanical and physical properties [1–3]. The confined environments of nanotubes permit the formation of unique encapsulated low dimensional structures with unusual properties compared with the bulk with possible applications as nano-catalysts, electronic devices and magnetic tapes [4, 5]. Most of the previously reported methods for the fabrication of these one-dimensional nanostructures involve multi-step processes, following CNT synthesis [6–8]. Various techniques have been developed for the synthesis of CNTs [9–11]. Thermal (catalytic) CVD still remain one of the dominant methods of their production. However, controlled growth of CNTs has always been a great challenge, which demands an efficient and reproducible route for catalyst preparation. Along with the synthesis of CNTs, filling of metal particles or binary alloy particles inside the CNTs has also been undertaken by various researchers [8, 12]. Here, the carbon shells provide an effective barrier against oxidation, which ensures a long-term stability of an individual nanowire, in contrast to most wires prepared from template-based methods. Metal encapsulated CNTs have also been studied for their fundamental interest, as CNTs can act as ideal nanosized pore for the study of confined materials and their filling has been shown to alter the physical properties of both the metals as well as CNTs [13]. In most previous reports, certain organometallic compounds containing Fe, Co and Ni have been used for the production of CNT encapsulated binary alloy nanowires [14, 15]. We have previously reported a simple and cost effective method to synthesize MWNTs in large yield and good purity by catalytic decomposition of acetylene using certain Zr based AB_2 and Mischmetal (Mm) based AB_2/AB_5 alloy hydride catalysts, prepared through hydrogen decrepitation technique [16–18]. These alloy hydride particles are catalytically very active, due to the presence of transition metals such as Fe, Co or Ni and are free from being oxidized due to their novel preparation

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technique. The thermo catalytic decomposition of methane has recently been receiving attention as an alternative route to the production of hydrogen from natural gas [19]. The hydrogen produced is free of carbon monoxide and the other products being tubular carbon. Results obtained on the generation of carbon monoxide-free hydrogen during the CVD growth process will also be discussed. In the present work, we discuss the synthesis of SWNTs, MWNTs and novel Zr based AB_2 alloy nanowire/Ni filled MWNTs with the generation of carbon monoxide-free hydrogen, by catalytic CVD of methane using Zr based AB_2 alloy hydride catalyst obtained through hydrogen decrepitation technique. Alloy nanowires with initial stoichiometry could be obtained with uniform filling inside the MWNT cavities. Furthermore, the catalysts being hydrogen storage alloys, we envisage that these novel structures could possibly be used as microelectrodes in fuel cell technology and H_2 sensors. We also discuss the growth of Ni encapsulated MWNTs, SWNTs using similar procedure, but at elevated temperatures. Thus, in this letter, a single step process is demonstrated for growing SWNTs, MWNTs and in situ Ni/ternary alloy filled MWNTs, along with the generation of CO-free hydrogen by using a suitable hydrogen decrepitated Zr based AB_2 alloy to pyrolyse methane at different reaction temperatures. These carbon nanostructures have been characterized by SEM, TEM, EDX, HRTEM and Raman spectroscopy.

The alloy hydride catalyst fine powers (~5–10 μm) were prepared through hydrogen decrepitation route by performing several cycles of hydrogenation/dehydrogenation of the alloy using a Seiverts apparatus [17]. The growth of carbon nanostructures has been carried out using a single-stage furnace at temperatures varying from 850 to 950°C. Fine powders of Zr based AB_2 alloy, obtained after several cycles of hydrogenation/dehydrogenation, was directly placed in a quartz boat and kept at the center of a quartz tube, which was placed inside a tubular furnace. Hydrogen (50 sccm) was introduced into the quartz tube for 1 h at 500°C, in order to remove the presence of any oxygen on the surface of the alloy hydride catalysts. Hydrogen flow was stopped and then furnace was heated up to the desired growth temperature followed by the introduction of methane with a flow rate of 100 sccm. All experiments were carried out for 30 min. Methane flow was stopped and the furnace was cooled to room temperature. Argon flow was maintained through out the experiment (1 bar, 200 sccm). Hydrogen generated was collected for 3 min at the outlet, after 5 min from the start of the experiment. The carbon soot obtained in the quartz boat was purified using acid treatment

and air oxidation [16] and were analysed by transmission electron microscopy (TEM) using a PHILIPS CM 200, operating at 200 kV, equipped with an EDX detector. Raman spectrum has been obtained from a Renishaw Raman spectrometer, using 514.5 nm excitation.

Different types of carbon nanostructures have been obtained from CVD of methane at different growth temperatures (850–950°C), using Zr based alloy hydride catalyst. Alloy-filled MWNTs were obtained at a growth temperature of 850°C, while Ni-filled MWNTs were observed at a slightly higher growth temperature (875°C). At 900°C, we obtained MWNTs. SWNTs were obtained at a higher growth temperature (950°C). Figure 1a shows the transmission electron microscopy (TEM) image of Zr-based AB_2 alloy filled MWNT, which was obtained with methane decomposition at 850°C. Uniform filling of the alloy has been observed inside the CNT cavity. A magnified TEM image of the alloy-filled MWNT is shown in Fig. 1b. An alloy nanowire of around 20 nm thickness is seen. We also obtained Ni-filled MWNTs using the same experimental conditions at slightly higher temperature (~875°C). A high resolution TEM (HRTEM) image of Ni-filled MWNT shows the monocrystallinity of Ni nanowire (Fig. 1c). At a growth temperature of 900°C, keeping the other CVD conditions same, we obtained MWNTs alone, without any metal/alloy filling (Fig. 1d). Energy dispersive X-ray analysis (EDAX) spectra of the alloy-filled MWNTs (Fig. 2a) showed the presence of Zr, Cr, Fe and Ni; the constituents of the alloy, with a composition comparable to that of the initial alloy used for the preparation of hydride catalysts. Figure 2b shows the EDX spectra of Ni-filled MWNT. TEM and HRTEM images of SWNTs obtained at a growth temperature of 950°C are respectively shown in Fig. 3a and b. It can be seen that SWNTs are of larger diameter of around 2 nm. Alloy filling inside SWNTs was not observed. The carbon yield during the deposition has been calculated as described previously [17] and a dependence of the yield of carbon with the growth temperature has been plotted and shown in Fig. 4. It could be seen that the carbon yield increased with increasing growth temperature and a maximum of around 146% has been obtained at 950°C for the carbon deposition, which corresponds to the growth of SWNTs. Raman spectroscopy has also been used to characterize these carbon nanostructures. Figure 5 shows the Raman spectra of SWNTs, Ni-filled MWNTs and MWNTs grown using decomposition of methane over Zr based AB_2 alloy hydride catalyst. For MWNTs, typical tangential modes corresponding to the Raman allowed

Fig. 1 (**a**) Low and, (**b**) high magnification TEM images of Zr-based AB$_2$ alloy filled MWNTs grown at a temperature of 850°C, (**c**) HRTEM image of Ni-filled MWNT grown at 875°C, (**d**) TEM image of MWNTs grown at 900°C
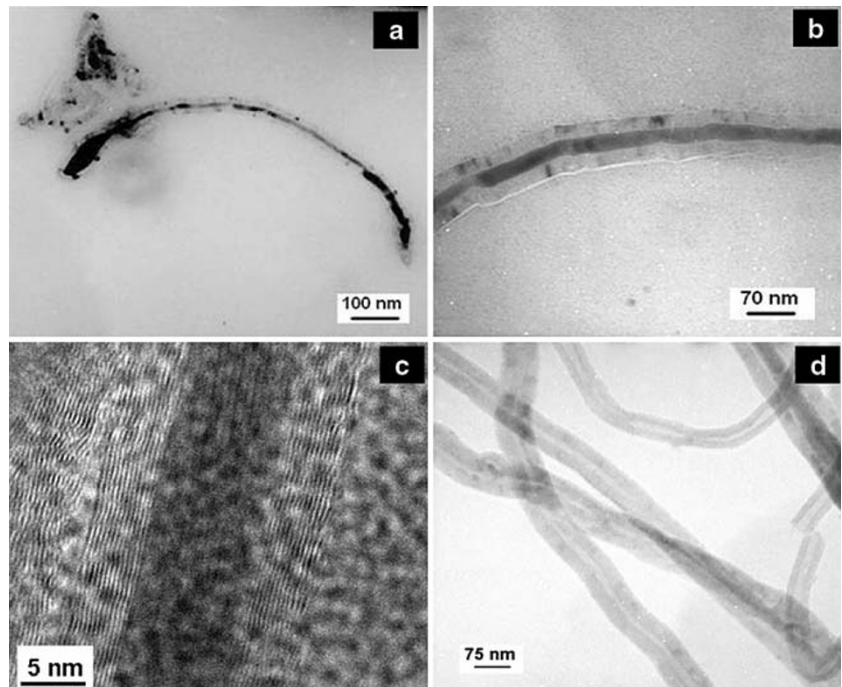
optical mode E$_{2g}$ of two-dimensional graphite, centered around 1589 cm^{-1} (G-band) [20] is observed. In addition, a peak centred at around 1367 cm^{-1} (D-
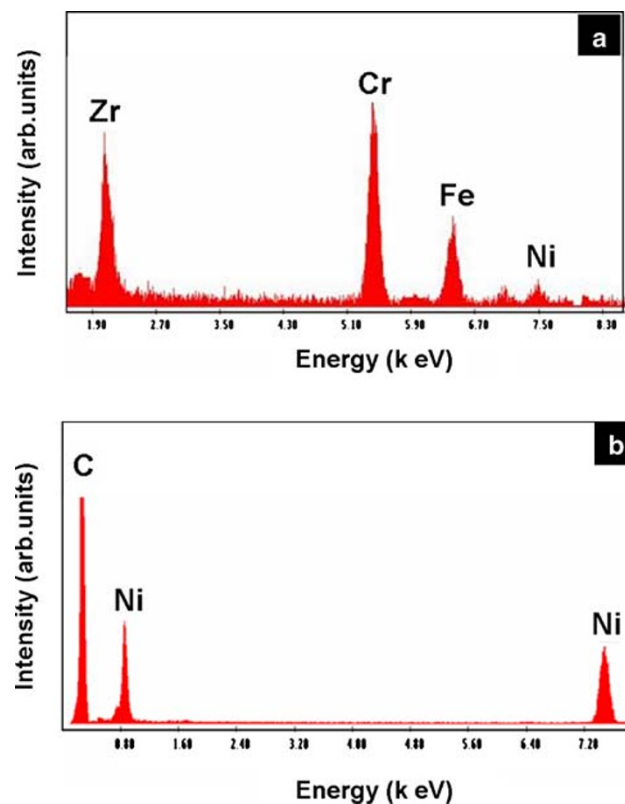

Fig. 2 EDAX spectra of (**a**) alloy filled MWNTs, and (**b**) Ni nanowire encapsulated MWNTs

band), mainly due to defects [20] is also observed. Raman spectra for SWNTs show the presence of RBM, at 388.9 cm^{-1}, in addition to the G- and D-bands. The increase in the intensity of D-band for Ni-filled MWNTs is due to the non-uniform filling of Ni, resulting in increased degree of disorderness.

Alloy nanowire filled MWNTs could be used in the development and fabrication of microelectrodes in fuel cell technology and as hydrogen sensors. Filling of hydrogen storage alloy nanowires inside CNTs prevents them from oxidation and hence results in their enhanced properties. Mischmetal (Mm) based AB$_2$ and AB$_5$ hydrogen storage alloys have also been used as catalysts for the growth of MWNTs [17]. Filling Mm based alloy inside the MWNTs would effectively reduce the cost factor and could as well be used in developing magnetic storage devices, and further work is in progress.

In the present study, as the size of the alloy hydride catalyst particles are seen to be in the range of 5–10 μm, we propose that each alloy hydride particle would be composed of a number of catalytic centres, which could act as nucleation sites for the growth of carbon nanotubes. There could be a further reduction in the catalyst particle size during the hydrogen treatment before the carbon deposition. Further, the nickel or iron particles are well interspersed in the alloy, allowing better dispersion of the active catalytic sites. This would further result in lesser sintering of the particles. Here, the possible growth mechanism could
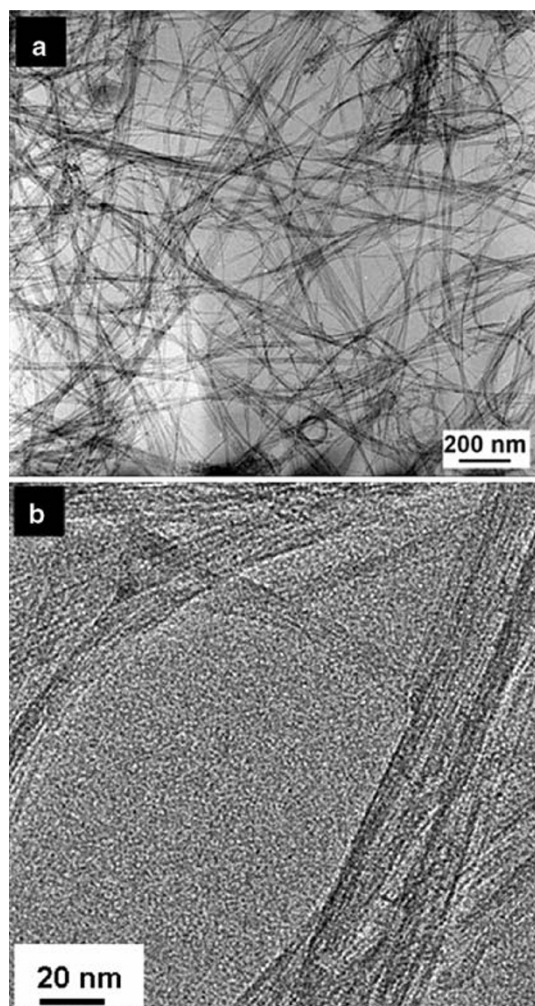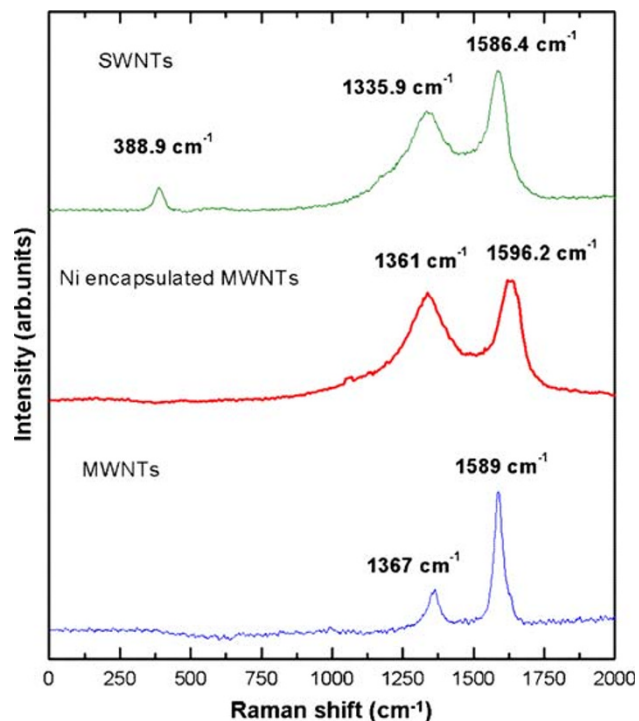
Fig. 3 (**a**) TEM, and (**b**) HRTEM images of SWNTs grown at 950°C
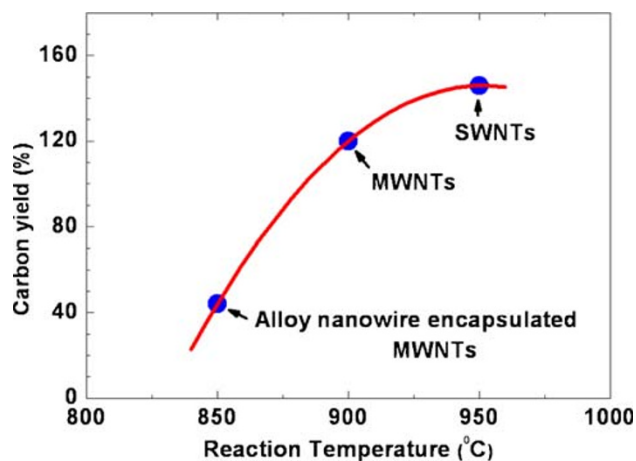
Fig. 4 Dependence of carbon yield on the reaction temperature

be through the precipitation of carbon in the form of MWNTs from the molten catalytic particles. The melting temperatures of the alloy-C system are lower
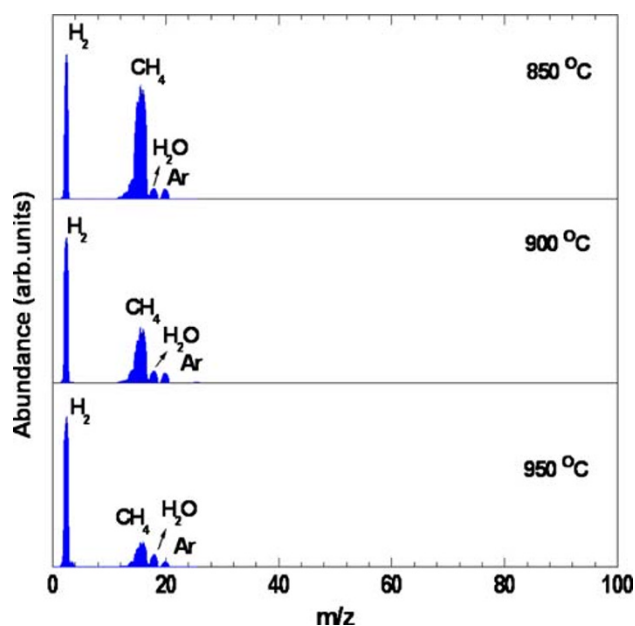

Fig. 5 Raman spectra of SWNTs, MWNTs and Ni-nanowire encapsulated MWNTs synthesized by the decomposition of methane over Zr based AB_2 hydride catalyst

than those of the metal-C system. Further, reduction in particle size results in lowering of melting temperature [21]. According to two widely accepted "tip-growth" and "root-growth" mechanisms, the hydrocarbon gas decomposes on the metal surfaces of the metal particle to release carbon, which dissolve in these metal particles. The dissolved carbon diffuses through the particle and gets precipitated to form the body of the filament. The saturated metal carbides have lower melting points. Hence, they are fluid like during the growth process resulting in their easy encapsulation due to the capillary action of the nanotube process. The encapsulated fluid results in solid metal nanowire. The thin alloy nanowire seen inside the MWNT cavity could be due to the solidified form of the liquid-phase alloy particle, suggesting that the growth process is by the vapour–liquid–solid (VLS) mechanism [22]. The novel approach to catalyst preparation using hydrogen decrepitation ensures increase in total surface area by providing fresh surfaces, which further enhance the catalytic reactivity and active sites for the formation of CNTs.

We have also analysed the outlet gas during methane decomposition at various temperatures and studied the generation of hydrogen. The outlet gas was collected in an evacuated round bottom (RB) flask

for 3 min, after 5 min from the start of the experiment. The gas collected at different deposition temperatures under the same experimental conditions have been analysed using mass spectroscopy. Figure 6 shows the mass spectra of the collected gas during methane decomposition over Zr based AB_2 alloy hydride catalyst at different temperatures varying from 850 to 950°C. The generation of hydrogen free from CO/CO_2 has been confirmed. While almost same amount of hydrogen was generated at different decomposition temperatures studied, it could be clearly seen that the residual unreacted hydrocarbon amount significantly reduced with increasing temperature. The peak corresponding to water is due to the moisture from the water trap used at the gas outlet of the CVD apparatus. Presence of small amount of argon is also seen. Hence, hydrogen with maximum purity was obtained at a decomposition temperature of 950°C, which corresponds to the deposition of SWNTs. Various bimetallic catalysts have been used as catalysts for the production of hydrogen [23]. Carbon nanofibers possessing a platelet structure were obtained by Wang et al., by decomposition of methane over Ni–Cu–MgO catalyst [24]. Since the morphology of deposited carbon and the methane decomposition rate depend on the structure and nature of the active catalytic sites and the size of the catalyst particles [21], alloy hydride catalysts with low cost and active catalytic centres would be desirable for the catalytic decomposition of methane to produce pure hydrogen.

In summary, we have demonstrated a single step controllable method for the synthesis of good quality and large quantity of Ni metal/ternary alloy nanowire-filled MWNTs, SWNTs and MWNTs in which alloy hydride particles obtained from hydrogen decrepitation technique have been used as catalysts [25]. The most unique advantage of this single-step process is that these one-dimensional nanostructures are grown in situ during the CVD process, which overcomes the limitation caused by the multi-step processes in existing methods. These alloy encapsulated MWNTs show potential applications in the field of spintronics, nano-electronics and sensors [26–29]. Generation of CO/CO_2-free hydrogen along with the CVD process has also been demonstrated. Maximum yield of carbon deposit and evolved hydrogen with maximum purity were obtained at a methane decomposition temperature of 950°C, which corresponds to the growth of SWNTs.

Fig. 6 Mass spectra analysis of the outlet gas during the methane decomposition at varying temperatures

References

1. B. Zhang, C. Liu, H.M. Cheng, Q.K. Cai, New Carbon Mater **18**, 174 (2003)
2. M. Terrones, N. Grobert, W.K. Hsu, Y.Q. Zhu, W.B. Hu, H. Terrones, J.P. Hare, H.W. Kroto, D.R.M. Walton, MRS Bull **24**, 43 (1999)
3. R.R. Meyer, J. Sloan, R.E. Dunin-Borkowski, A.I. Kirkland, M.I. Novotny, S.R. Bailey, J.L. Hutchison, M.L.H. Green, Science **289**, 1324 (2000)
4. G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher, Langmuir **15**, 750 (1999)
5. J. Sloan, J. Cook, M.L.H. Green, J.L. Hutchison, R. Tenne, J. Mater. Chem. **7**, 1089 (1997)
6. J.C. Bao, C. Tie, Z. Xu, Z.Y. Suo, Q.F. Zhou, J.M. Hong, Adv. Mater. **14**, 1483 (2002)
7. J.C. Bao, Q.F. Zhou, J.M. Hong, Z. Xu, Appl. Phys. Lett. **81**, 4592 (2002)
8. D. Golberg, C.Z. Gu, Y. Bando, M. Mitome, C.C. Tang, Acta. Mater. **53**, 1583 (2005)
9. D.S. Bethune, C.H. Kiang, M.S. deVries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature **363**, 605 (1993)
10. T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. **243**, 49 (1995)
11. M. Yudasaka, R. Kikuchi, R. Matsui, Y. Ohki, S. Yoshimura, E. Ota, Appl. Phys. Lett. **67**, 2477 (1995)
12. J.P. Cheng, X.B. Zhang, F. Liu, J.P. Tu, Y. Ye, Y.J. Ji, C.P. Chen, Carbon **41**, 1965 (2003)
13. Y. Gao, Y. Bando, D. Goldberg, Appl. Phys. Lett. **81**, 4133 (2002)
14. N. Grobert, M. Terrones, O.J. Osborne, H. Terrones, J. Olivares, W.K. Hsu, S. Trasobares, Y.Q. Zhu, J.P. Hare, H.W. Kroto, D.R.M. Walton, Appl. Phys. A **67**, 595 (1998)
15. C.N.R. Rao, R. Sen, B.C. Satishkumar, L. Govindaraj, Chem. Commun. **15**, 1525 (1998)

16. M.M. Shaijumon, S. Ramaprabhu, Chem. Phys. Lett. **374**, 513 (2003)
17. M.M. Shaijumon, N. Rajalakshmi, H. Ryu, S. Ramaprabhu, Nanotechnology **16**, 518 (2005)
18. M.M. Shaijumon, N. Bejoy, S. Ramaprabhu, Appl. Surf. Sci. **242**, 192 (2005)
19. L. Piao, Y. Li, J. Chen, C. Liu, J.Y.S. Lin, Catal. Today **74**, 145 (2002)
20. R. Saito, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)
21. A.A. Moisala, G. Nasibulin, E.I. Kauppinen, J. Phys: Condens. Matter. **15**, S3011 (2003)
22. I.C. Leu, M.H. Hon, Y.M. Lu, J. Electrochem. Society **146**, 184 (1999)
23. Y.D. Li, J.L. Chen, Y.N. Qin, L. Chang, Energy Fuels **14**, 1188 (2000)
24. H.Y. Wang, R.T.K. Baker, J. Phys. Chem. B **108**, 20273 (2004)
25. S. Ramaprabhu, M.M. Shaijumon, Patent filed (No:1129/CHE/05)
26. I. Mönch, A. Meye, A. Leonhardt, K. Krämer, R. Kozhuharova, T. Gemming et al., J Magn Magn Mater. **290**, 276 (2005)
27. G. Korneva, H.H. Ye, Y. Gogotsi, D. Halverson, G. Friedman, J.C. Bradley, K.G. Kornev, Nano Lett. **5**, 879 (2005)
28. C. Müller, S. Hampel, D. Elefant, K. Biedermann, A. Leonhardt, M. Ritschel, B. Büchner, Carbon **44**, 1746 (2006)
29. C.K. Yang, J. Zhao, J.P. Lu, Phys. Rev. B. **90**, 257203 (2003)