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**Pyrolytic Synthesis of Carbon Nanotubes from Sucrose on a Mesoporous
Silicate**

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Abstract

Multiwall carbon nanotubes were synthesized from sucrose by a pyrolytic technique using mesoporous MCM-41 silicate templates without transition metal catalysts. The Nanotubes were examined in the carbon/silicate composite and after dissolution of the silicate. High resolution transmission electron microscopy study of the multiwall nanotubes showed them to be 15 nm in diameter, 200 nm in length and close-ended. There was variation in crystallinity with some nanotubes showing disordered wall structures.

1. Introduction

The discovery of carbon nanotubes by Iijima in 1991 [1] has been followed by enormous interest and many studies of properties, structures and synthesis methods. Nanotubes have been suggested for a variety of applications because of unique electronic, mechanical and chemical properties, including: advanced scanning probes,¹ electron field emission sources,² hydrogen storage materials,³ and building blocks of molecular electronics.^{4,5} CNTs have extraordinary mechanical properties and carbon nanotube reinforcements have the potential for production of high-strength composites with properties well-suited for aerospace applications. There are, at this time, well known synthesis procedures for production of both multiwall (MWNT) and singlewall (SWNT) nanotubes [6]. The near-term commercialization of nanotube devices would benefit from production of tubes of high purity, and uniform morphology, in large volumes at a reasonable cost.

Many methods of nanotube production rely on the use and incorporation of transition metal catalysts. These techniques require a subsequent, costly, purification treatment to obtain high quality nanotubes. In this study we have only considered methods of production of nanotubes produced without the use of metal catalysts. Furthermore, we evaluate the use of an inexpensive precursor, sucrose, which is an agricultural commodity available at pennies per pound.

There have been many recent advances in a field of chemistry known as “single molecule” chemistry, where three dimensional space is compartmentalized into small, usually nanometer-sized subunits or “nanoreactors.” [7] within molecular sieves. Molecular sieves are ordered, porous structures, with nanometer-scale pores, and include the naturally occurring zeolites. Because of their crystalline nature, pores of the same type are precisely the same size. Depending on the size of the pores, they can selectively adsorb or filter different molecules, thus functioning as molecular sieves.

A very useful family of mesoporous molecular sieves was reported by Mobil company researchers 1992 [8-10], and designated the M41S types. The structure of one of these materials, MCM-41 (Mobil Composite Material – 41) has been completely resolved, and consists of parallel channels ordered into a 1-d hexagonal honeycomb array. The synthesis of this class of materials is based on a cooperative self-assembling of inorganic and organic components in a precursor mixture into a liquid crystalline mesophase. The MCM-41 mesophase consists of parallel, hexagonally ordered cylindrical surfactant micelles, with a surface covered by inorganic anions. Polymerization results in rigid channel walls, and a high temperature treatment removes the organic component, leaving a porous aluminosilicate. The pores of the molecular sieves can be tailored within a range of 2 to 10 nm uniform cylindrical pores (vs. 4 Å - 15 Å for conventional zeolites). Another M41S aluminosilicate, MCM-48 has a cubic structure (*Im3d*) and exhibits a 3D, interconnecting channel system [11-13]

Recent studies have revealed a method for production of nanotubes of uniform morphology through the use of molecular sieve templates. SWNT have been grown from carbonization of template molecules of tripropylamine (TPA) which were used for synthesis of $\text{AlPO}_4\text{-5}$ (AFI) type zeolite [14-19]. The nanotubes were extremely thin and superconductive. The SWNT were examined within the zeolite. Measurements of the SWNT/zeolite composite revealed the inner diameter of the AFI crystal channels to be 0.73 nm. Consideration of the Van der Waals radius of carbon suggested a diameter of 0.4nm for the nanotubes [18]. This type of very thin SWNT were found to be unstable when removed from the zeolite, especially under the electron beam of the TEM [14].

Ryoo et al. [20] used sucrose as a carbon source with a mesoporous sieve template to produce ordered carbon/silicate composite sieves and carbon molecular sieves. MCM-48 was impregnated with sucrose and sulfuric acid in aqueous solution and heated to 1073-1373 K under vacuum or in an inert atmosphere. Sucrose was converted to carbon using sulfuric acid as the catalyst. The XRD pattern taken prior to the framework removal was identical to that of the

the silica template MCM-48 except for lattice contraction and intensity loss. The contraction has been observed to occur when the MCM-48 structure is subjected to high temperature. The intensity loss was attributed to the pores filling with carbon. Subsequent removal of the silica template with HF or NaOH solution resulted in a carbon molecular sieve. XRD results showed a transformation of structural symmetry from that of the silicate [21]. When SBA-15 was used as a template, the symmetry was retained after silicate digestion, and this was attributed to the greater interconnection of the tubes by micropores within the pore walls [22]. Recent work has suggested similar approaches for the production of carbon nanotubes [23].

Multiwall carbon nanotubes (MWNT) have been reported to be synthesized by using mesoporous MCM-41 and MCM-48 silicates as nanoreactors in the absence of metal catalysts [24-30]. This was done by two methods. In one case the structure directing organic molecules were transformed into carbon nanotubes; no additional carbon source was added. The MCM-41 precursor was heat-treated in nitrogen at 1073 K for 30 minutes. This served to pyrolyze the organic component into graphitized carbon. The silicate was then dissolved in HF, and carbon nanotubes were collected. In another method, divinylbenzene was infiltrated into the pores of MCM-41 and MCM-48. Graphitization occurred after heating for 5 - 30 minutes at 1073 K. Removal of the silicate by dissolution in either 38% HF or 10 M NaOH produced nanotubes which could be observed by TEM. The carbon nanotubes generated from the divinylbenzene source were less graphitized, with a disordered wall structure. For both of these synthesis methods the diameter of the tubes was found to be significantly larger than the original pore diameter of the silicate. Carbonization of templates in mesitylene expanded EXMCXM-41 sample gave carbon nanotubes of top quality [27].

2. Experimental

The following method was used for the synthesis of a monolithic carbon-silicate (MCS) nanocomposite and the release of carbon nanotubes (CNTs) by dissolution of the silicate. The synthesis was performed using the hexagonal mesoporous silica molecular sieve MCM-41 as a template and sucrose as the carbon source.

Reagents used for the synthesis included NH_4OH (30 wt. %), Tetraethylorthosilicate (TEOS), aluminum isopropoxide $[(\text{iso-pro})_3\text{Al}]$ and Cetyltrimethylammonium bromide (CTABr) (Aldrich). The synthesis of the silica mesoporous materials was performed using the following reaction composition 1.0 TEOS: 0.01 $[(\text{iso-pro})_3\text{Al}]$: 0.2 CTABr: 0.5 NH_4OH : 150 H_2O . The resulting gel was aged for 3 days at 110 °C in Teflon-lined stainless steel autoclaves. The product was filtered, washed with distilled water, dried in air and then calcined at 650 °C for 6h.[28,29] The resulting Al-MCM-41 materials were impregnated twice with sucrose dissolved in sulfuric acid. The mixture was dried at 160 °C in nitrogen atmosphere. The resulting products were heated at 780 °C under vacuum for 9h. The sucrose was thus converted to carbon using sulfuric acid as the catalysts. The resulting composite is referred to as MCS.

X-ray powder diffraction (XRD) patterns were obtained on a Siemens diffractometer equipped with a rotating anode and $\text{Cu-K}\alpha$ radiation (wavelength $\lambda=0.15418$ nm).

Samples of carbon nanotubes were prepared for high resolution electron microscopy (HREM) examination by digestion in a 1:1 solution of concentrated $\text{HF}:\text{H}_2\text{O}$ for 12 hours, followed by dilution, and rinsing. The filtrate was then suspended in methyl alcohol and pipetted unto lacey formvar/carbon films supported by copper grids (Pella 01881-F). The specimens were then allowed to dry at room temperature for several hours. They were examined in a Philips

CM200 SuperTwin transmission electron microscope (TEM), operated at 200 kV accelerating voltage. High Resolution TEM Images were collected via a Gatan Imaging Filter system (GIF) using a 10 eV slit over the zero loss, 200 keV beam. Images were processed by addition of the original image to the filtered inverse fast fourier transform to enhance contrast of periodic features. Electron energy loss spectra (EELS) were collected for a 30 nm probe positioned on a cluster of MWNT.

3. Results

The XRD patterns of template (substituted-MCM-41) (Figure 1) have a sharp d_{100} reflection with additional 110, 200 and 210 reflections indicative of a long range ordered hexagonal framework. The XRD of MCS nanocomposites was the same as that for the templates except for lattice contraction and some intensity loss. Lattice contraction usually occurs when the substituted-MCM-41 is subjected to heating at high temperature even without sucrose [30], while the intensity loss can be attributed to the pore filling with carbon. Removal of the silicate templates by HF produced material which showed no Bragg diffraction in the small-angle region.

TEM study of the MCS nanocomposite (Figure 2) showed pore to pore dimensions in of ~ 5.3 nm, measured from the end view of the hexagonal array.

The HF digested filtrate was examined by TEM. Multiwalled carbon nanotubes (MWNT) were observed, although the volume fraction within the filtrate was not very large. A thin, amorphous film was observed on the MWNT surface, which increased in thickness during TEM observation. The MWNT averaged about 15 nm in diameter (after subtraction of the amorphous film) and about 200 nm in length. HRTEM images in Figures 3a and 3b show a range of crystallization of the nanotube. The walls of the tubes in Figure 3b are much more linear, whereas the tube in Figure 3a shows significant wall curvature. Two distinct features are

notable in Figure 3b: a double MWNT, and an internal, possibly growth fault. Figure 3c shows the closed ends of two adjoined MWNT. The EELS spectrum in Figure 3d shows the near edge structure of the carbon core loss peak, with a small, π^* peak due to the sp^2 hybridization characteristic of the graphitic bonding of carbon nanotubes.

4. Discussion

MWNT have been observed by TEM after pyrolysis of sucrose in a transition-metal-free, mesoporous template and after dissolution of the carbon/silicate composite. The yield from the conditions examined was not great. Additionally, the MWNT were significantly larger in diameter than the pores of the template material within which they are presumed to have developed. We have to consider three possibilities to explain this apparent discrepancy: 1) swelling of the MWNT after dissolution of the template, 2) the addition of artifact structures during preparation of the sample and 3) the growth of MWNT external to the porous substrate.

The first case has been suggested by other researchers. In the case of the thin, 0.4 nm SWNT formed within AFI pores, dissolution resulted in development of graphite onions and small pieces of “graphite stripes”, which were concluded to have resulted from the instability of the SWNT outside of the template structure. Large MWNT were reported by Urban et al. [24], with diameters indicated by HREM to be about 8 – 10 nm, after growth in 3 nm pores (measured by nitrogen adsorption). In the current study, the MWNT were about 15 nm in diameter, and associated with similarly sized pores.

The possibility of TEM examination of artifacts has been addressed by Klie, et al. [31]; particularly for low-yield experiments. They indicated that amorphous carbon films made by d.c. arc-discharge contain a relatively high density of graphitic structures that can be easily mistaken for the genuine sample

structures. The carbon support films used for this study were purchased from a commercial supplier, Pella, as lacey carbon/formvar films. Based on the comments above, an hours-long examination of bare films was undertaken and revealed a small amount of graphite, but no carbon nanotubes. The artifact question can be handled in future studies by use of carbon-free support films or grids for the study of carbon nanomaterials, as suggested by Klie, et al. [31] and Reed and Sarikaya [32].

The final possibility, of external growth, is worth comment. We noted growth of highly aligned, parallel structures, which are likely to have been joined during growth. The two MWNT shown in Figure 3b are an example. The internal cavity diameter of the MWNT is a better match with the MCM-41 pore size. External growth, on the surface of the mesoporous silicate would facilitate joining of the MWNT during growth, since there would be no intermediate silicate material. However, TEM examination of the MCS nanocomposite, Figure 2, did not reveal any external growth. A more thorough study of the MCS material may answer that question.

All three of these explanations remain possible and should be considered in future studies of similar processes. Our observation of MWNT growth from a mesoporous silicate, in the absence of metal catalysts, shows similar results to work published by other groups.

Figure 1. XRD

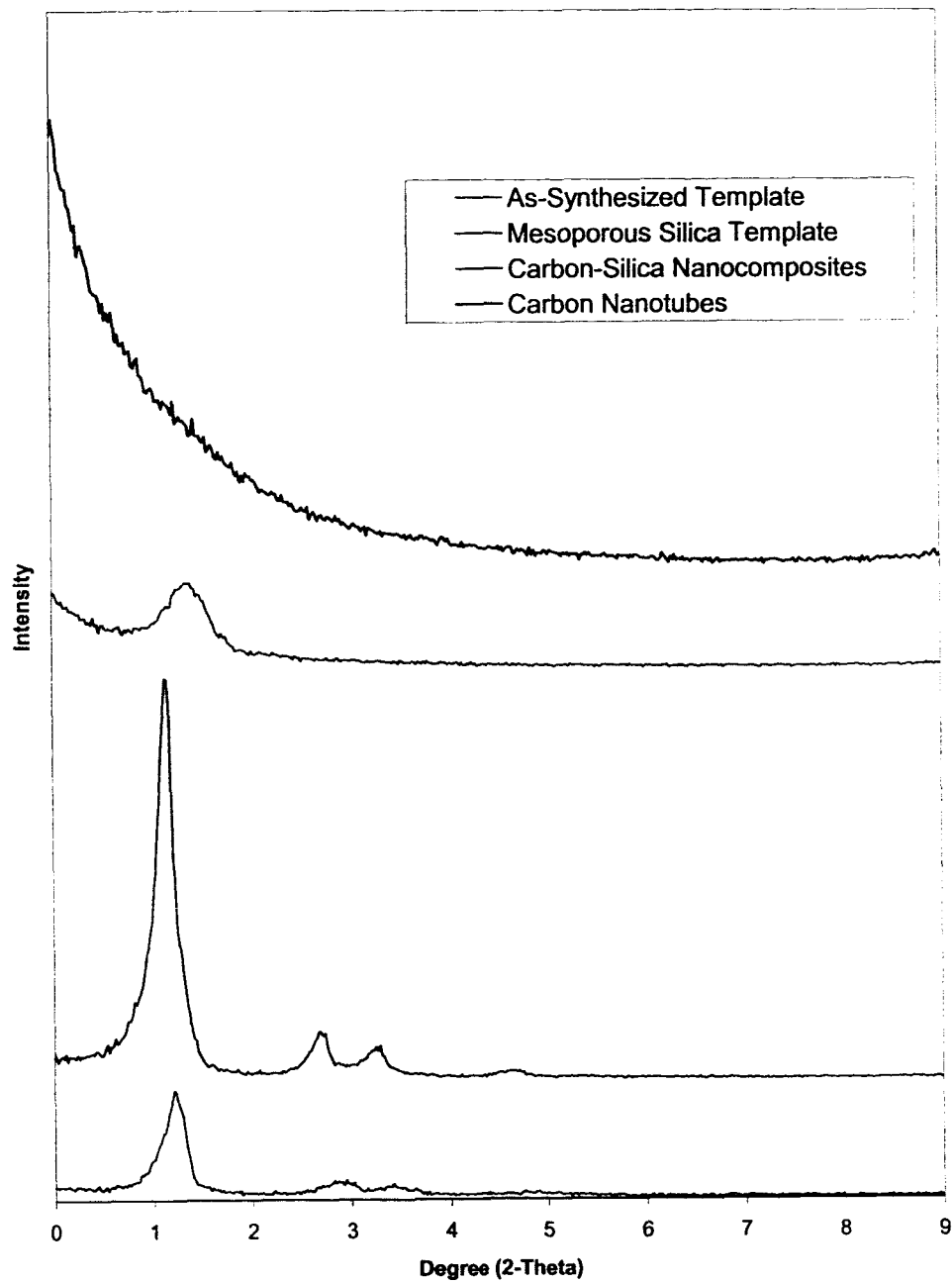


Figure 1. X-ray diffraction data from MCM-41 and MCS.

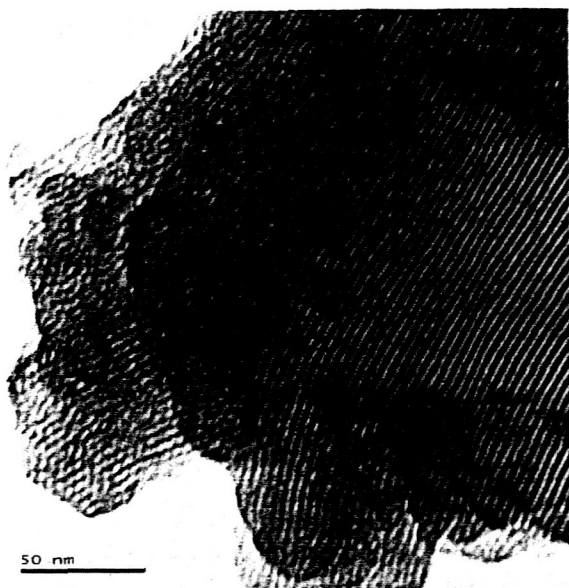
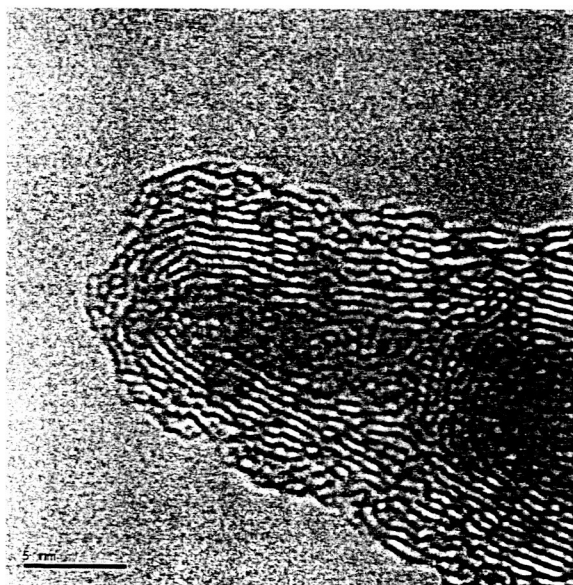
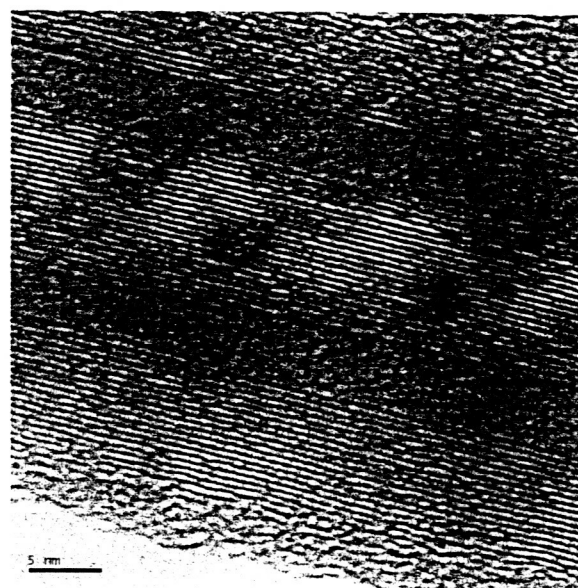
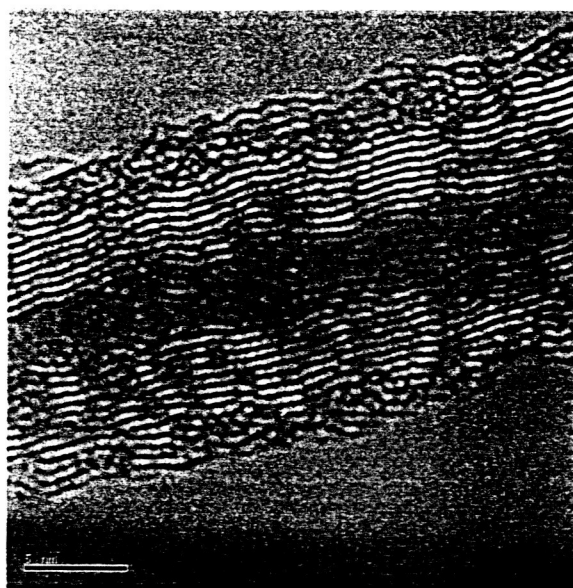


Figure 2. TEM of MCM-41/Carbon composite, pore spacing 5.3 nm, center-to-center.



50 eV

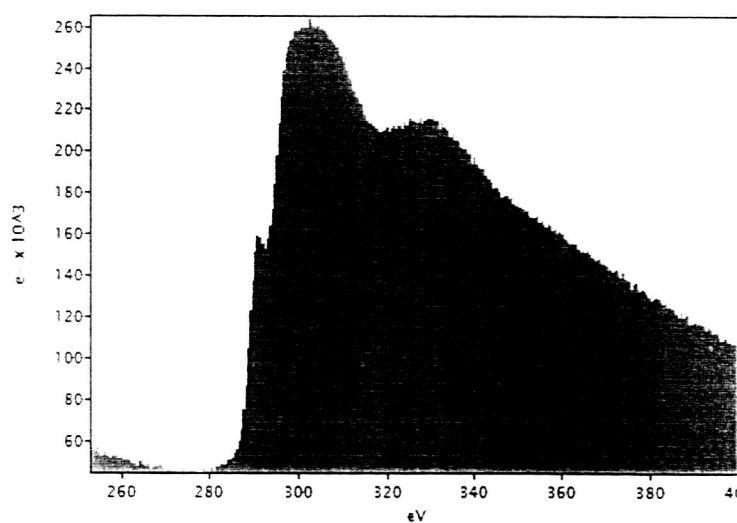


Figure 3. MWNT. a) disordered wall structure of ~ 12 nm diameter MWNT, not fully graphitized; b) closed-end of two adjoining MWNT (note amorphous layer on MWNT surface); c) wall structure of two overlapping MWNT showing better graphitization; d) EELS of C K-edge, with π^* peak showing sp^2 hybridization of graphite.

References

- (1) Dai, H., Hafner, J. H.; Rinzler, A. G.; Colbert, D. J.; Smalley, R. E. *Nature* **1996**, *384*, 147-150.
- (2) Choi, W. B.; Chung, D. S.; Kang, J. H.; Kim, H. Y.; Jin, Y. W.; Han, I. T.; Lee, Y. H.; Jung, J. E.; Lee, N. S.; Park, G. S.; Kim, J. M. *Appl. Phys. Lett.* **1999**, *75*, 3129-3131.
- (3) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127.
- (4) DePablo, P. J.; Graugnard, E.; Walsh, B.; Andres, R. P.; Datta, S.; Reifenger, R. *Appl. Phys. Lett.* **1999**, *74*, 323-325.
- (5) Wei, Y. Y.; Eres, G. *Appl. Phys. Lett.* **2000**, *76*, 3759-3761.
6. C. Journet and P. Bernier; "Production of carbon nanotubes," *Appl. Phys. A* **67**, 1998., 1-9.
7. M. Antonietti and K. Landfester, "Single Molecule Chemistry with Polymers and Colloids: A Way to Handle Complex Reactions and Physical Processes?", *ChemPhysChem* **2001**, *2*, 207-210.
8. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker,; *J.Am.Chem.Soc.* **114**, 1992, 10834.
9. J.S. Beck, K.D. Smith, J.C. Vartuli; U.S. Patent 5,334,368.
10. J.S. Beck, C.T. Kresge, S.B. McCullen, W.J. Roth, J. C. Vartuli; U.S. Patent 5,370,785.
11. G. Van Tendeloo, O.I. Lebedev, O. Collart, P. Cool and E.F. Vansant; "Structure of nanoscale mesoporous silica spheres," *J.Phys.: Condens. Matter* **15**, 2003, S3037-S3046.
12. P.I. Ravikovitch and A.V. Neimark; *2000 Langmuir*, **16**, 2419.
13. K. Schumacher, P.I. Ravikovitch, A. Du Chesne, A. H. Neimark and K.K. Unger; *2000 Langmuir*, **16**, 4648.
14. Z.K. Tang, H.D. Sun, J. Wang, J. Chen, and G. Li, *Appl. Phys. Lett.*, **73** no. 16, 1998, 2287-2289.

15. H.D. Sun, Z.K. Tang, J. Chen, and G. Li, Appl. Phys. A 69, 1999, 381-384.
16. H.D. Sun, Z.K. Tang, and J.N. Wang; J. Magn. Magn. Mat., 198-199, 1999, 255-257.
17. Z.K. Tang, L. Zhang, N. Wang, X.X., Zhang, G.H. Wen, G.D. Li, J.N. Wang, C.T. Chan, P. Sheng; Science, 292, 2462-2465.
18. N. Wang, G.D. Li, Z.K. Tang; Chem. Phys. Let. 339, 2001, 47-52.
19. A. Jorio, A.G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, A. Righi, F.M. Matinaga, M.S.S. Danta, M.A. Pimenta, J. Mendes Filho, Z.M. Li, Z.K. Tang, R. Saito, Chem. Phys. Let. 351, 2002, 27-34.
20. R. Ryoo, S.H. Joo, S. Jun; "Synthesis of Highly Ordered Carbon Molecular Sieves via Template-Mediated Structural Transformation," J. Phys. Chem. B, 103 (37), 1999, 7743-7746.
21. S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki; J. Am. Chem. Soc. 122, 2000, 10712-10713.
23. F. Kleitz, S.H. Choi, R. Ryoo; "Cubic Ia3d large mesoporous silica: synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes," Chem. Commun., 2003, 2136-2137.
24. M. Urbán, Z. Konyá, D. Méhn, J. Zhu and I. Kiricsi; "Mesoporous silicates as nanoreactors for synthesis of carbon nanotubes," PhysChemComm, 5(20), 2002 138-141.
25. M. Urbán, D. Méhn, Z. Konyá, J. Zhu and I. Kiricsi; "Production of carbon nanotubes inside the pores of mesoporous silicates," Chemical Physics Letters 359, 2002, 95-100.
26. M. Urbán, Z. Konyá, D. Méhn, J. Zhu and I. Kiricsi; "Mesoporous silicates as nanoreactors for carbon nanotube production in the absence of transition metal catalysts," J. Nanosci. Nanotechnol. 3(1-2), 2003, 111-119.
27. M. Urbán, D. Méhn, Z. Konyá, J. Zhu and I. Kiricsi; "Production of multiwall carbon nanotubes in the modified pore system of mesoporous silicates," Diamond and Related Materials, 13, 2004, 1322-1326.
28. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J.C.; Beck, J.S. *Nature* 1992, 359,710.

29. Beck, J. S.; Vartuli, J.C.; Routh, W. J.; Leonowitz, M.E.; Kresge, C.T.; Schmitt, K.D.; Chu, C.T.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* 1992, *114*, 10834.
30. Abdel-Fattah, T. M.; Pinnavaia, T. J. *Chem. Commun.* 1996, 665.
31. R.F. Klie, D. Ciuparu, L. Pfefferle, Y. Zhu; "Multi-walled carbon nanotubes on amorphous carbon films," *Carbon* 42, 2004, 1953-1957.
32. B. Reed and M. Sarikaya; "TEM/EELS analysis of heat-treated carbon nanotubes: experimental techniques," *Journal of Electron Microscopy* 51, 2002, S97-S105.