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Synthesis of Carbon Nanotubes

Near-Quantitative Solid-State Synthesis of Carbon Nanotubes from Homogeneous Diphenylethynecobalt and –Nickel Complexes**

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Carbon nanotubes (CNTs) have generated a tremendous amount of research interest because of their unique structural, electronic, magnetic, and mechanical properties.[1] Among the various synthetic methods employed for their preparation, chemical vapor deposition (CVD) has emerged to be most effective, and efforts are increasing in applying this technique to pre-growth device fabrication by utilizing (in particular lithographically)[2] patterned catalyst arrays and in situ tube assembly.[2,3] Crucial in this endeavor is the site-specific batch production of ordered carbon with control of stoichiometry and ultimately morphology. One possible approach to achieving this would be the efficient thermal conversion of a defined, soluble, molecular organometallic precursor composed of both the carbon source and the metal catalyst, placed locospecifically by wetting and drying. Such a strategy would combine the advantages of the floating organometallic catalyst (for example, ferrocene, $[Fe(CO)_5]$, etc.) CVD methodology[1d,4] with a solid-state conversion of carbon precursors. Reports of the latter reveal some serious shortcomings with respect to yield and/or degree of graphitization, extremity of conditions, need for specialized equipment, the requirement of co-reagents, and simplicity of starting materials.[1d,5] We have described the solid-state thermolysis of a $[Co_2(CO)_6]$-complexed tetrabenzodehydro[20]annulene and some of its substructures to form ordered carbon material, but this method shared some of these drawbacks, in as much as the highest yields were only about 60%. The desired product consisted of an (at best) approximately equal mixture of multiwalled tubes (MWNTs)

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and carbon onions, and the starting alkyne ligands were somewhat esoteric.[6] We now disclose a qualitative and quantitative breakthrough in the execution of this strategy, which has potential utility in applications to device construction.

Our previous work[6] suggested a pronounced effect of the precursor alkyne–metal structure on the effectiveness of conversion and selectivity. Consequently, a program was instituted to evaluate a range of metal complexes of alkynylbenzenes of initially increasing and then decreasing complexity. Remarkably, while all of the former and most of the latter (such as $[Co_2(CO)_6]$ complexes of ethynylbenzene and diphenylbutadiyne), produced only amorphous, graphitic, and, occasionally, minor quantities of tube- and onionlike carbon in varying proportions, the diphenylethyne complex $[Co_2(CO)_6(PhC_2Ph)]$ (**1**), which is readily prepared in one step from commercial materials,[7] behaved dramatically differently. Thus, heating **1** (30–60 mg) in a quartz tube ($d =$ 1 cm, $l = 15$ cm) sealed under vacuum to 650 °C for 1.5–2 h, or after a wash with conc. HCl, gave samples of metal-encapsulating, pure MWNTs as thin, free-standing films of "nano(bucky)paper",[8] which turned to a black powder on sonication in 2-propanol or grinding (Figure 1 a,c,d). A representative TEM micrograph of this material is shown in Figure 1 b, which reveals for the first time the typical, dense nanotube pattern that is normally only obtainable using gas-phase techniques. Other forms of ordered and amorphous carbon could not be found. The tubes, on average, exceeded 5 μm in length, with many extending to 20 μm, and exhibited a narrow (inner-outer) diameter distribution of 15–40 nm. The tubes contained 20–50 layers, of which the inner 60–80 % were well graphitized while the outer regions exhibited lesser (turbostratic) ordering (high-resolution transmission electron microscopy (HRTEM); Figure 2 a).

Gravimetric analysis of the crude carbon material before the acidic wash established a 64 % mass recovery, and elemental analysis furnished a carbon content of 60.26 %, which is consistent with a product of composition $C_{15}Co_2$ (calcd mass recovery 64% and C content 60.45 %). Acid treatment removed most, but not all, of the metal (60 % mass recovery, elemental analysis: C 89.50 %, calcd for $C_{42}Co$: C 89.54 %). Indeed, most of the tubes contained a crystalline fcc arrangement of cobalt atoms (by energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and HRTEM),[9] usually at random positions and occasionally at the tips (Figure 2 b),[10] and are ferromagnetic.[9c,11]

The process can be scaled up to 2-g batches using stainless steel Swagelock fittings containing **1** loaded in a glove box. This procedure produced chunks (not films) of lesser quality tubes that were contaminated with carbon onions and graph-

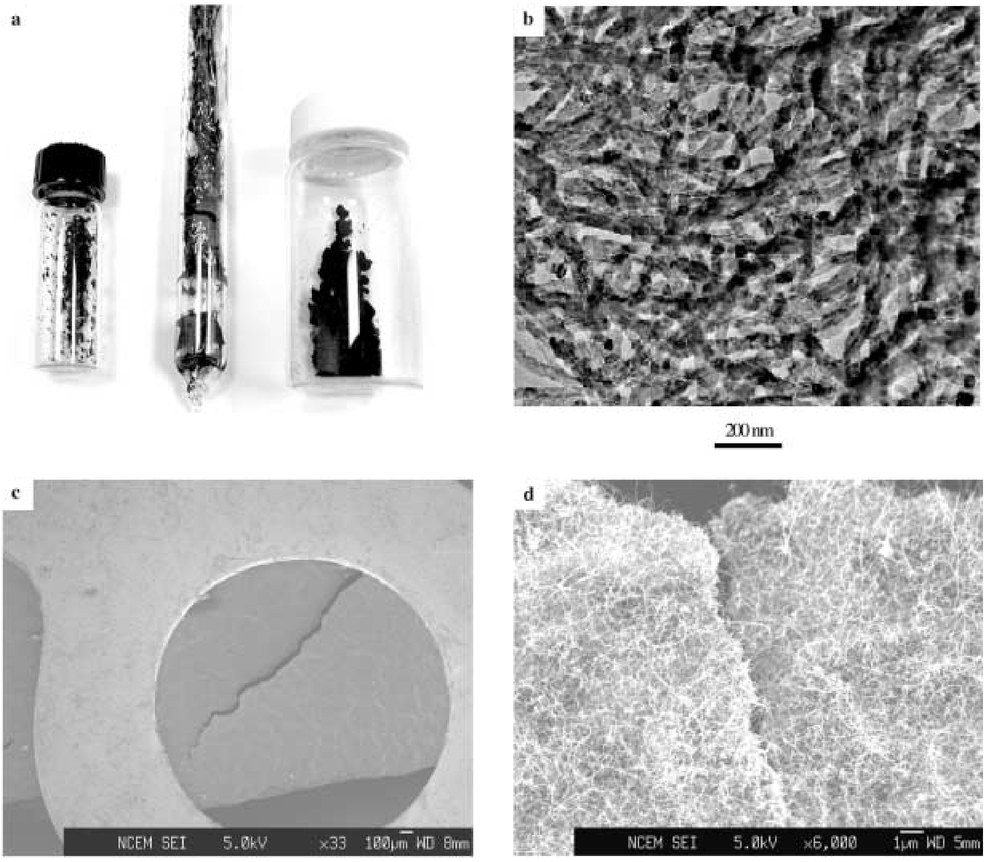

Figure 1. a) A sample of crystalline **1** (left), thermolyzed to a film of carbon tubes (middle), and then treated with conc. HCl and ground to a powder of MWNTs (right). b) TEM micrograph of the as-produced MWNT. Some of the dark spots represent an fcc arrangement of cobalt particles. c) SEM micrograph at lower magnification showing an SEM sample holder with a purposely torn piece of nanopaper. d) The tear in (c) at larger magnification.

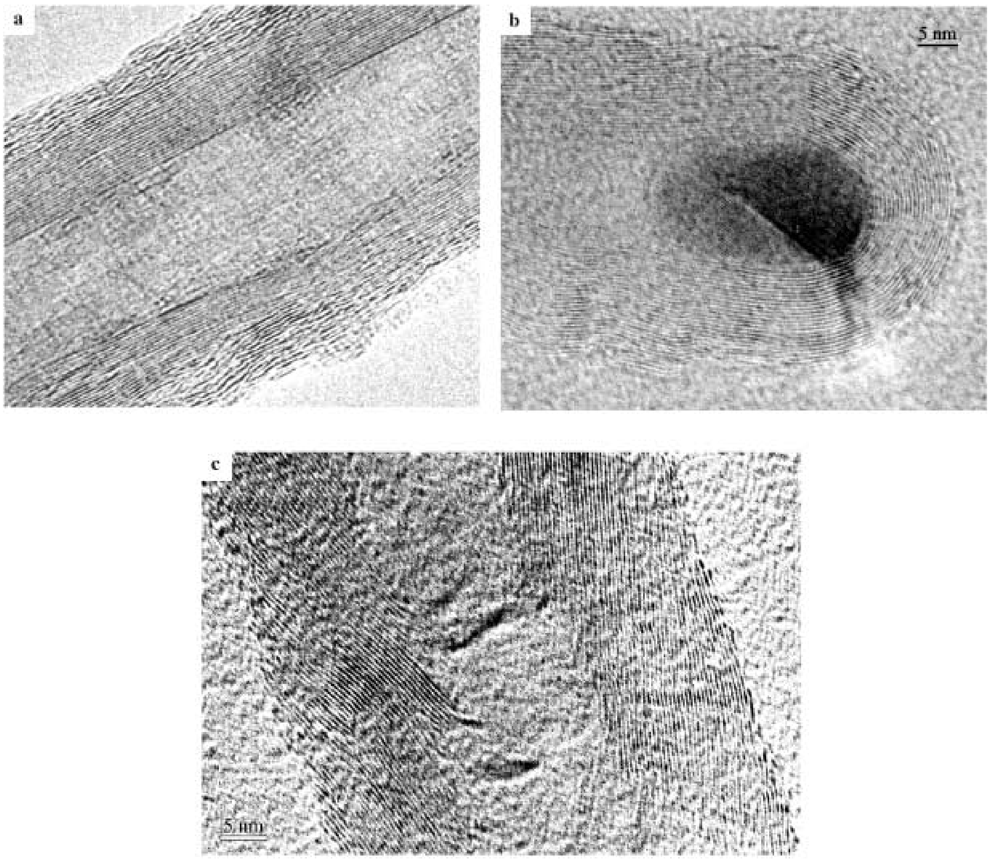

Figure 2. a) Typical segment of a MWNT obtained from the thermolysis of **1**. b) MWNT tip containing an fcc arrangement of cobalt atoms; Co fringes 0.203 nm, graphitic fringes 0.340 nm. c) Typical herringbone NTs from **1** and hexaphenylbenzene (HRTEM: Topcon 002B, 120 keV; SEM: Jeol 6340F; EDS: Phillips CM200 at 120 keV; XRD: Bruker AXS D8).

ite. More successfully, it can be turned moderately "catalytic" in **1**, in as much as up to three equivalents of ligand are tolerated, before a significant deterioration in the yield and quality of the nanotubes is observed. We suspected that the added ligand was cyclotrimerized[12] before further annealing, and **1** could also be admixed with up to one equivalent of hexaphenylbenzene to produce good quality tubes in high yields. However, in all cases, increasing the amount of external carbon sources resulted in the tubes becoming shorter, their diameter more variable, and, their morphology changing to that of a herringbone motif (Figure 2 c).[13] Other sources of carbon added to **1**, such as pentaphenylcyclopentadiene, C_{60}, C_{70}, anthracene, and ethynylbenzene, had a detrimental effect. On the other hand, performing the same set of experiments with $[Ni(cod)_2]/PhC_2Ph$ (**2**, 1:1; cod = cycloocta-1,5-diene),[14] a pyrophoric mixture prepared in the pyrolysis tubes at −80 °C, provided essentially identical (positive and negative) results: free-standing films of MWNTs (post acidic wash: elemental analysis: C 89.56 %, calcd for $C_{42}Ni$: C 89.58 %) that were equally well graphitized, but with a larger (outer) diameter distribution of 40–90 nm, and containing a crystalline fcc arrangement of Ni atoms (Figure 3).[15] Again, the ratio of alkyne to metal complex could be increased successfully to 3:1 to provide a carbon yield based on the metal of $>1000\,\%$, which compares favorably with CVD results.[16]

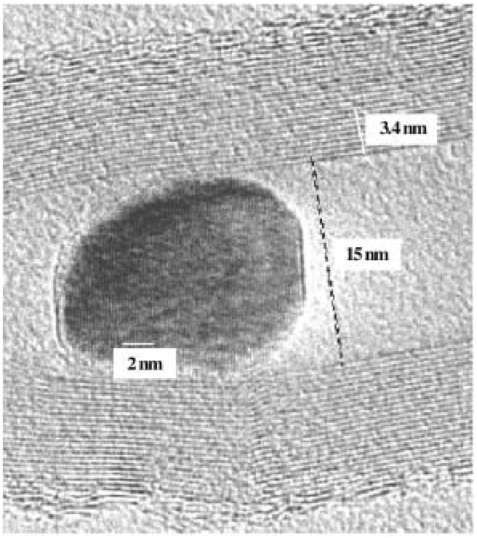

Figure 3. Portion of a typical CNT from **2** with a crystal containing an fcc arrangement of Ni atoms.

Preliminary investigations of the scope of this method are promising. Thus, while the addition of sulfur-containing compounds to **1** (elemental sulfur, thiophene, thianaphthene)[1] resulted in only amorphous carbon and onionlike assemblies, the addition of one equivalent of $[Mo(CO)_6]$[17] or $[Mo(CO)(PhC_2Ph)_3]$[18] to **1**, followed by pyrolysis, generated MWNTs of narrower diameter and with fewer walls (3–5). Single-wall nanotube (SWNT) bundles[19] were also formed with some tubes encapsulating fullerenes ("pea pods"),[20] all unfortunately only in low yields (Figure 4). Unlike any of the other systems investigated by us, the MALDI-TOF mass spectra of the soot revealed C_x peaks up to m/z 3000. Finally, an attempt to obtain SWNTs by using MgO-supported[21] **1**, followed by dissolution of the support (HCl), surprisingly led instead to extensively aligned free-standing MWNT bundles (HRTEM).[22]

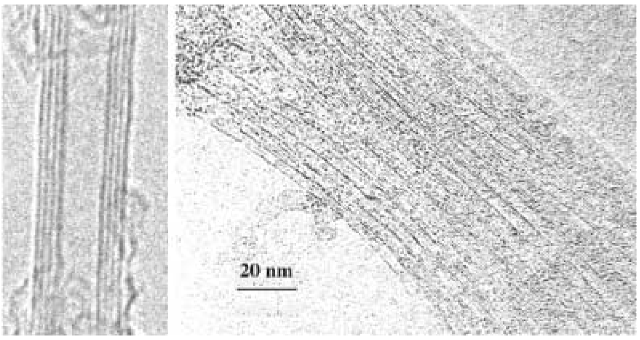

Figure 4. Selected four-walled NT from a mixture of **1** and the Mo complex (1:1; left). Selected SWNT bundles obtained from the same mixture (right). These structures were not quantified and yields are diminished by the presence of amorphous carbon and less graphitized materials.

In summary, we have presented an efficient, solid-state conversion of commercial homogeneous organometallic systems with a defined metal to carbon ratio into metal-crystallite-encapsulating MWNTs with a high carbon yield based on the metal. While not competitive with large-scale CVD processes, it may complement existing methods and lead to new methods of device construction, such as designed networks and hybrid materials, and may be useful in other applications.[23] Moreover, the molecular nature of the starting materials provides an opportunity for tailoring and mechanistic scrutiny (by, for example, in situ TEM).

Experimental Section

A sample of **1** (46 mg, 0.1 mmol) was sealed under Ar (partial pressure 20 mTorr) in a quartz tube at −80 °C, and then the tube was heated to 650 °C for 2 h to yield a black film of crude soot. The product was gently ground into a fine powder, washed with conc. HCl, and a sample (ca. 0.1 mg) dispersed in 2-propanol and sonicated for 1 min. A drop of this dispersion was placed on a holey carbon TEM grid and analyzed by recording images from 20000 to 690000 magnification (Topcon 002B, 120 keV).

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[1] For selected recent reviews, see a) H. Dai, *Surf. Sci.* **2002**, *500*, 218; b) R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787; c) C. N. R. Rao, B. C. Satishkumar, A. Govindaraj, M. Nath, *ChemPhysChem* **2001**, *2*, 78; d) E. G. Rakov, *Russ. Chem. Rev.* **2000**, *69*, 35.

[2] For recent studies, see a) H. Dai, *Acc. Chem. Res.* **2002**, *35*, 1035; b) S. Huang, X. Cai, J. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 5636; c) B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanth, P. M. Ajayan, *Chem. Mater.* **2003**, *15*, 1598; d) B. Wang, X. Liu, H. Liu, D. Wu, H. Wang, J. Jiang, X. Wang, P. Hu, Y. Liu, D. Zhu, *J. Mater. Chem.* **2003**, *13*, 1124; e) G. S. Duesberg, A. P. Graham, M. Liebau, R. Seidel, E. Unger, F. Kreupl, W. Hoenlein, *Nano Lett.* **2003**, *2*, 257; f) H. C. Choi, S. Kundaria, D. Wang, A. Javey, Q. Wang, M. Rolandi, H. Dai, *Nano Lett.* **2003**, *2*, 157; g) B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanth, P. M. Ajayan, *Nature* **2002**, *416*, 495; h) X. Wang, Y. Liu, P. Hu, G. Yu, K. Xiao, D. Zhu, *Adv. Mater.* **2002**, *14*, 1557; i) S. Huang, L. Dai, A. W. H. Mau, *Adv. Mater.* **2002**, *14*, 1140; j) S. Huang, L. Dai, *J. Nanopart. Res.* **2002**, *4*, 145, and references therein.

[3] See also, for example, a) S. Orlanducci, V. Sessa, M. L. Terranova, M. Rossi, D. Manno, *Chem. Phys. Lett.* **2003**, *367*, 109, and references therein; b) Z. Pan, H. Zhu, Z. Zhang, H. Im, S. Dai, D. B. Beach, D. H. Lowndes, *J. Phys. Chem. A* **2003**, *107*, 1338; c) J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, *Appl. Phys. Lett.* **2003**, *82*, 2491; d) R. Vajtai, K. Kordás, B. Q. Wei, J. Békési, S. Leppävuori, T. F. George, P. M. Ajayan, *Mater. Sci. Eng. C* **2002**, *19*, 271.

[4] For reviews, see a) C. N. R. Rao, A. Govindaraj, *Acc. Chem. Res.* **2002**, *35*, 998; b) A. Govindaraj, C. N. R. Rao, *Pure Appl. Chem.* **2002**, *74*, 1571; for very recent studies, see, for example, c) C. Singh, M. S. P. Shaffer, K. K. K. Koziol, I. A. Kinloch, A. H. Windle, *Chem. Phys. Lett.* **2003**, *372*, 860; d) H. Hou, A. K. Schaper, Z. Jun, F. Weller, A. Greiner, *Chem. Mater.* **2003**, *15*, 580; e) L. Ci, H. Zhu, B. Wei, C. Xu, D. Wu, *Appl. Surf. Sci.* **2003**, *205*, 39; f) Z. Zhang, B. Wei, P. M. Ajayan, *Chem. Commun.* **2002**, 962; g) X.-Y. Liu, B.-C. Huang, N. J. Coville, *Carbon* **2002**, *40*, 2791; h) P. C. P. Watts, W. K. Hsu, D. P. Randall, V. Kotzeva, G. Z. Chen, *Chem. Mater.* **2002**, *14*, 4505; i) T. Katayama, H. Araki, K. Yoshino, *J. Appl. Phys.* **2002**, *91*, 6675.

[5] For illustrative references, see a) S. P. Doherty, D. B. Buchholz, B.-J. Li, R. P. H. Chang, *J. Mater. Res.* **2003**, *18*, 941; b) M. Laskoski, W. Steffen, J. G. M. Morton, M. D. Smith, U. H. F. Bunz, *J. Am. Chem. Soc.* **2002**, *124*, 13814; c) H. Liu, Y. Li, L. Jiang, H. Luo, S. Xiao, H. Fang, H. Li, D. Zhu, D. Yu, J. Xu, B. Xiang, *J. Am. Chem. Soc.* **2002**, *124*, 13370; d) Y. Lu, Z. Zhu, W. Wu, Z. Liu, *Chem. Commun.* **2002**, 2740; e) S. P. Doherty, R. P. H. Chang, *Appl. Phys. Lett.* **2002**, *81*, 2466; f) D. Sarangi, C. Godon, A. Granier, R. Moalic, A. Goullet, G. Turban, O. Chauvet, *Appl. Phys. A* **2001**, *73*, 765; g) J. L. O'Loughlin, C.-H. Kiang, C. H. Wallace, T. K. Reynolds, L. Rao, R. B. Kaner, *J. Phys. Chem. B* **2001**, *105*, 1921; h) L. Ji, J. Lin, H. C. Zeng, *Chem. Mater.* **2000**, *12*, 3466.

[6] a) P. I. Dosa, C. Erben, V. S. Iyer, K. P. C. Vollhardt, I. M. Wasser, *J. Am. Chem. Soc.* **1999**, *121*, 10430; see also b) R. Boese, A. J. Matzger, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1997**, *119*, 2052.

[7] H. Pepermans, R. Willem, C. Hoogzand, *Bull. Soc. Chim. Belg.* **1987**, *96*, 563.

[8] The term "buckypaper" was coined for material derived from SWNTs. For potential uses, see, for example, a) A. Minett, J. Fràysse, G. Gang, G.-T. Kim, S. Roth, *Curr. Appl. Phys.* **2002**, *2*, 61; b) J. Li, A. Cassell, L. Delzeit, J. Han, M. Meyyappan, *J. Phys. Chem. B* **2002**, *106*, 9299; c) A. Guiseppi-Elie, C. Lei, R. H. Baughman, *Nanotechnology* **2002**, *13*, 559; d) J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *J.

Am. Chem. Soc. **2001**, *123*, 6536; e) D. F. Johnson, B. J. Craft, S. M. Jaffe, *J. Nanopart. Res.* **2001**, *3*, 63.

[9] See, for example, a) V. Lavrentiev, H. Abe, S. Yamamoto, H. Naramoto, K. Narumi, *Surf. Interface Anal.* **2003**, *35*, 36; b) J. p. Pinheiro, M. C. Schouler, E. Dooryhee, *Solid State Commun.* **2002**, *123*, 161; c) R. K. Rana, X. N. Xu, Y. Yeshurun, A Gedanken, *J. Phys. Chem. B* **2002**, *106*, 4079.

[10] Assuming a liquid catalytic particle growth mechanism, it appears that under our conditions random migration of the metal occurs after growth termination. For recent, relevant references, see, for example, a) O. A. Louchev, *Phys. Status Solidi A* **2002**, *193*, 585; b) J. Gavillet, A. Loiseau, F. Ducastelle, S. Thair, P. Bernier, O. Stéphan, J. Thibault, J.-C. Charlier, *Carbon* **2002**, *40*, 1649; c) A. Gorbunov, O. Jost, W. Pompe, A. Graff, *Carbon* **2002**, *40*, 113, and references therein.

[11] See, for example, a) J. Harujama, I. Takesue, T. Hasegawa, *Appl. Phys. Lett.* **2002**, *81*, 3031; b) G. H. Lee, S. H. Huh, J. W. Jeong, H.-C. Ri, *J. Magn. Magn. Mater.* **2002**, *246*, 404.

[12] W. Hübel, C. Hoogzand, *Chem. Ber.* **1960**, *93*, 103.

[13] See, for example, M. Ritschel, M. Uhlemann, O. Gutfleisch, A. Leonhardt, A. Graff, C. Täschner, *Appl. Phys. Lett.* **2002**, *80*, 2985, and references therein.

[14] E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day, A. B. Anderson, *J. Am. Chem. Soc.* **1978**, *100*, 2090.

[15] Ascertained by EDS and XRD as in: a) O. M. Gur'yanova, E. F. Kukovitsky, S. G. L'vov, N. A. Sainov, V. A. Shustov, *Phys. Solid State* **2002**, *44*, 473; b) Y. K. Chen, A. Chu, J. Cook, M. L. H. Green, P. J. F. Harris, R. Heesom, M. Humphries, J. Sloan, S. C. Tsang, J. F. C. Turner, *J. Mater. Chem.* **1997**, *7*, 545.

[16] See, for example, a) A. K. M. Fazle Kibria, Y. H. Mo, K. S. Nahm, M. J. Kim, *Carbon* **2002**, *40*, 1241; b) I. Willems, Z. Kónya, J.-F. Colomer, G. Van Tendeloo, N. Nagaraju, A. Fonseca, J. B. Nagy, *Chem. Phys. Lett.* **2000**, *317*, 71; c) P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *313*, 91.

[17] CVD of $[Mo(CO)_6]$ furnishes MWNTs: M. Motiei, J. Calderon-Moreno, A. Gedanken, *Chem. Phys. Lett.* **2002**, *357*, 267.

[18] T. Szymańska-Buzar, T. Głowiak, *J. Organomet. Chem.* **1994**, *467*, 223.

[19] For bimetallic catalysis of SWNT synthesis with Co/Mo, see, for example, W. E. Alvarez, B. Kitiyanan, A. Borgna, D. E. Resasco, *Carbon* **2001**, *39*, 547, and references therein.

[20] For a review, see a) M. Monthioux, *Carbon* **2002**, *40*, 1809; see also b) B. W. Smith, R. M. Russo, S. B. Chikkannanavar, D. E. Luzzi, *J. Appl. Phys.* **2002**, *91*, 9333.

[21] Co/MgO converts CH_4 into single (or double) WNTs, but ethyne to MWNTs: a) P. Hu, X. Wang, Y. Liu, B. Wang, D. Zhu, *Synth. Met.* **2003**, *135–136*, 833; b) E. Flahaut, R. Bacsa, A. Peigney, C. Laurent, *Chem. Commun.* **2003**, 1442; c) Y. Soneda, L. Duclaux, F. Béguin, *Carbon* **2002**, *40*, 955; d) L. Quingwen, Y. Hao, C. Yan, Z. Jin, L. Zhongfan, *J. Mater. Chem.* **2002**, *12*, 1179, and references therein.

[22] For a review, see A. Huczko, *Appl. Phys. A* **2002**, *74*, 617.

[23] The materials produced from **1** show catalytic activity in the Pauson–Khand reaction and Fischer–Tropsch synthesis, those from **2** in the hydrogenation of nitroarenes.

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