



CVD synthesis of high-purity multiwalled carbon nanotubes using CaCO_3 catalyst support for large-scale production

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Abstract

Multiwalled carbon nanotubes (MWCNTs) were synthesized in a catalytic reaction using CaCO_3 as catalyst support. Impregnated with conventional catalysts CaCO_3 enabled the production of MWCNTs in a fixed-bed flow reactor at relatively low reaction temperature. The purification was performed in one step: both metallic particles and catalyst support were dissolved in a diluted acid. Hence, disadvantages, namely multi-step processes and hazardous chemicals, were avoided. A further advantage of CaCO_3 support is efficient and stable growth of MWCNTs. First results obtained in our new rotary-tube oven indicated high quality and pure MWCNTs with a yield of 100 g/day by this method.

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1. Introduction

Carbon nanotubes (CNTs) discovered by Iijima in 1991 are in the focus of material sciences [1]. For practical applications, large-scale production and high purity are essential. Among the various techniques of CNT synthesis, the electric arc-discharge method often yields high-quality CNTs, however, with a large amount of undesirable carbonaceous byproducts (amorphous carbon,

nanoparticles, fullerenes, etc.). Several methods have been tried to purify the soot. For instance, different oxidation techniques can remove polyhedral particles but unfortunately they destroy the overwhelming part of the sample and the end caps [2,3]. A non-destructive method has been carried out for arc-discharge CNTs in a colloidal suspension of nanoparticles stabilized with surfactants, followed by centrifugation and filtration [4,5]. Separation methods based on chromatography gives CNTs with high purity but they are nevertheless not suitable for purification of large amounts [6].

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Catalytic decomposition of carbon-containing compounds has been considered to be an appropriate method for the synthesis of CNTs in large quantities [7]. Numerous catalyst materials, as well as carbon sources have been tried out [8–11]; many promising results have been published underlining good selectivity, flexibility and technical simplicity [12,13]. The choice of the supporting material has been found to be critical for the scalable chemical vapor deposition (CVD) as well [14–17]. In particular, recent results based on silicagel- or zeolite-supported catalysts [14–16] made evident that porous materials are excellent supports in catalytic nanotube production. However, their purification still remains problematic [18,19] and requires a multi-step purification [20] which can damage the structure of products. Therefore, an important approach for the large-scale production of high-quality CNTs is (i) to keep the amount of contaminants as low as possible during the catalytic reaction, (ii) to use rather diluted mineral acids for purification and (iii) to reduce the number of purification steps. In this Letter, we present a new-type catalyst support for multiwalled CNT (MWCNT) growth, which enables a growth with high efficiency and purity. The subsequent purification is a one-step procedure, simple and harmless to the CNT structure, therefore, promising for large-scale and low-cost production of CNTs for industrial applications.

2. Experimental

MWCNTs were synthesized in the catalytic decomposition of acetylene at 720 °C over catalysts supported by CaCO_3 . As catalysts, mono-metallic salts of Co(II), Fe(II) and Fe(III) were applied as well as the bimetallic combination Fe(II),Co(II) and Fe(III),Co(II). To be precise, a calculated amount of metal salt ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and/or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{Fe}(\text{CH}_3\text{COO})_2$) was dissolved in distilled water and subsequently CaCO_3 was suspended into the solution for the catalyst preparation. The total concentration of catalysts was about 5 wt%. During the whole synthesis of the catalysts, the pH-value of the suspension was kept constantly at about 7.2 by

adding ammonia solution. The resulting mixture was placed in a beaker on a hot plate and the solvent was evaporated under continuous stirring. The as-prepared sample was dried at 120 °C overnight and then collected as dry powder.

The decomposition of acetylene was carried out in a fixed-bed flow reactor at 720 °C. Approx. 50 mg of the prepared supported catalysts (Co/ CaCO_3 , Fe(II)/ CaCO_3 , Fe(III)/ CaCO_3 , Fe(II),Co/ CaCO_3 or Fe(III),Co/ CaCO_3) was placed in a quartz boat which was inserted in a quartz tube under nitrogen flow. Keeping a continuous nitrogen flow of 70 l/h, acetylene was let through with a gas flow of 10 ml/min for 30 min. After rinsing the system with nitrogen, reaction product was collected from the quartz boat. Our standard fixed-bed flow reactor contains a reaction quartz tube of 18 mm diameter and a quartz boat of 12 mm diameter, the length of the heated area measures 200 mm.

Since the capacity and the scalability of the fixed bed reactor are limited, we elaborated a continuous production method based on a rotary tube furnace. A photograph of the installed oven is shown in Fig. 1. The oven has an 80 mm diameter rotating quartz tube with a heating area of 750 mm length. It is equipped with two reservoirs, one containing the catalyst and the other collecting the product. The catalyst is introduced into the reaction tube by gentle motor-driven shaking of the feeder. The rotation of the reaction tube and its inclination are manually set so that the speed of the catalyst passing through the heated zone can be varied, where the decomposition of acetylene takes place. All other processes such as heating, cooling and gas switching are automatically controlled. Finally, the product is collected at the lower end of the tube.

For purification, raw MWCNT samples were sonicated (30 Watt) in diluted nitric acid (30% HNO_3) for 30 min at room temperature, filtered, washed with distilled water acid-free and finally dried at 120 °C overnight. Diluted nitric acid was used in surplus amount to dissolve catalyst particles. Concerning the stoichiometry of the reaction, 1 g of CaCO_3 reacts with 1.26 g of nitric acid. The latter amount can be found in approx. 4 cm³ 30% nitric acid. Multiple volumes of that are certainly



Fig. 1. View of the rotary tube oven used for large-scale synthesis of CVD nanotubes. Inset shows the raw product of MWCNTs after one day of production in the reaction tube.

sufficient to dissolve both the catalyst particles and the support. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetry analysis (TGA) were carried out to characterize all samples. The latter was carried out in nitrogen atmosphere or in air (Derivatograph-Q, MOM), in particular to monitor the weight losses of the catalysts at the temperature of CVD and the thermal stability of purified samples. TEM and SEM were used to characterize the CNT samples, in particular, to verify the yield, the wall structure and the purity of the samples. The TEM sample preparation involved grinding the synthesized material mechanically and gluing the ground powder on a Cu TEM-grid. For the TEM study, Philips CM20 and CM300 microscopes were used for conventional and high-resolution mode operating at 200 and 300 kV, respectively. Both microscopes were equipped with an energy-dispersive X-ray (EDX) detector for chemical analysis. SEM micrographs were taken using a Philips XL 30 FEG.

3. Results and discussion

Figs. 2a–c show representative TEM micrographs of carbon deposits grown on the surface of supported Co, Fe(III), and Fe(III),Co catalysts,

respectively. A high density of CNTs can be found, which cover thickly the catalyst particles. For all prepared samples, comparable yield was obtained except for Fe(II)/CaCO₃, which was sparsely or not at all covered with CNTs. Furthermore, detailed TEM investigation revealed that the samples contained solely CNTs, catalyst particles and support, while no amorphous carbon or carbonaceous particles was found. High-resolution TEM confirmed that CNTs were free of amorphous carbon; neither loosely bound clusters nor a thin layer attached to the outer surface of CNTs could be observed. The CNT wall structure was found well graphitized with a few defects characteristic for CVD synthesis. Fig. 2d illustrates a typical MWCNT grown using Fe(III),Co/CaCO₃ catalyst in high magnification. The image indeed demonstrates the well-graphitized wall structure without any indication of amorphous carbon coverage. Hence, our results clearly suggest that CaCO₃ is an eminent support for different catalysts, mono- or bimetallic. Moreover, it avoids the formation of carbonaceous byproducts and yields selective MWCNT formation with high efficiency.

The carbon yield, which was calculated from the ratio between the deposited carbon weight and the initial catalyst weight multiplied by 100, was in average 30%. Basically, CaCO₃ of powdered aragonite decomposes at about 825 °C. Indeed, we

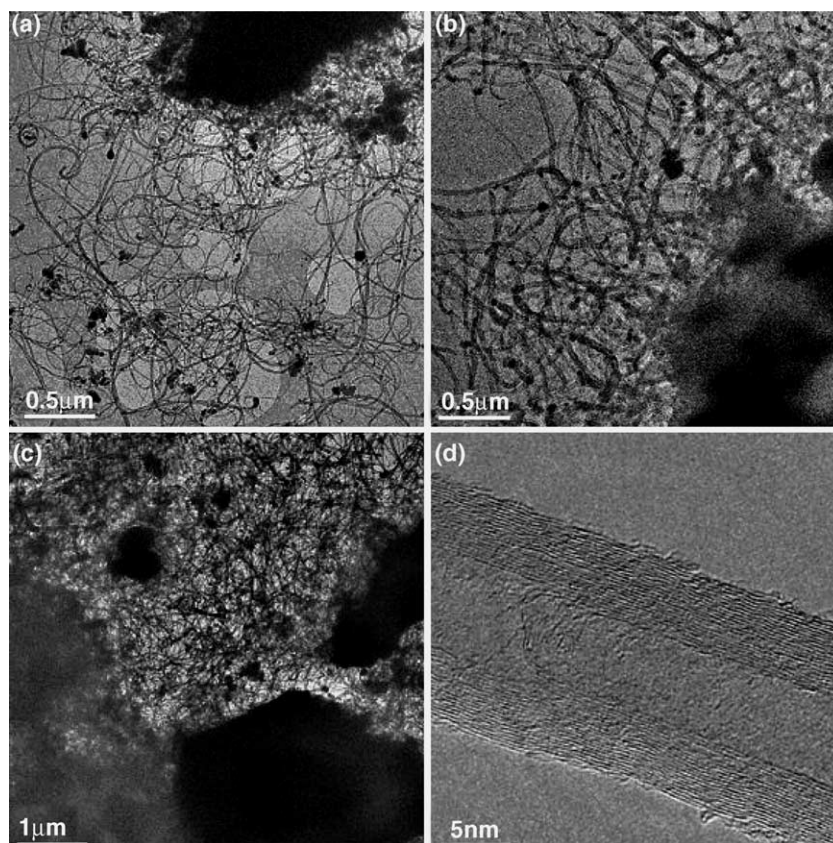


Fig. 2. Low magnification TEM micrographs of carbon nanotubes grown on the surface of CaCO_3 supported catalysts (a) Co, (b) Fe(III), and (c) Fe(III),Co. The catalyst particles and support material, which show dark contrast, are thickly covered with CNTs for all catalyst-types. No amorphous carbon or carbonaceous particles can be found. (d) High-resolution TEM image of a CNT observed in the sample shown in (c). The walls of pristine nanotube are well graphitized and no amorphous carbon attaches on the outer surface of the tubules.

observed in the TGA performed in nitrogen atmosphere a minor weight-loss at lower temperatures, which mainly originated from water removal in an endothermic process (up to 300 °C) and from decomposition of acetate at 330 up to 420 °C. Disintegration of CaCO_3 occurred between 700 and 900 °C and lead to a weight loss of 15%. However, during instantaneous heating of catalysts at 720 and 750 °C in the fixed-bed flow CVD oven and in the large-scale rotary tube, respectively, we observed a much higher weight loss which we attribute to the decomposition of CaCO_3 into CaO and CO_2 . Hence, after MWCNT synthesis the main side-product was CaO, which is soluble in diluted acids.

Fig. 3a displays a representative SEM micrograph of CNTs grown using Fe(III),Co catalysts supported by CaCO_3 before purification. This image confirms once more the high density of CNTs obtained using CaCO_3 support. A significant amount of particles is present, which are catalyst particles and support as found by TEM studies. In our system, diluted mineral acids such as nitric acid can dissolve these catalyst particles and the support material. Indeed, the amount of particles is significantly reduced after purification without any noticeable destruction of CNTs, as can be seen in Fig. 3b. TEM micrographs of purified CNTs, which were grown using Fe(III), Co catalysts supported by CaCO_3 , are shown in

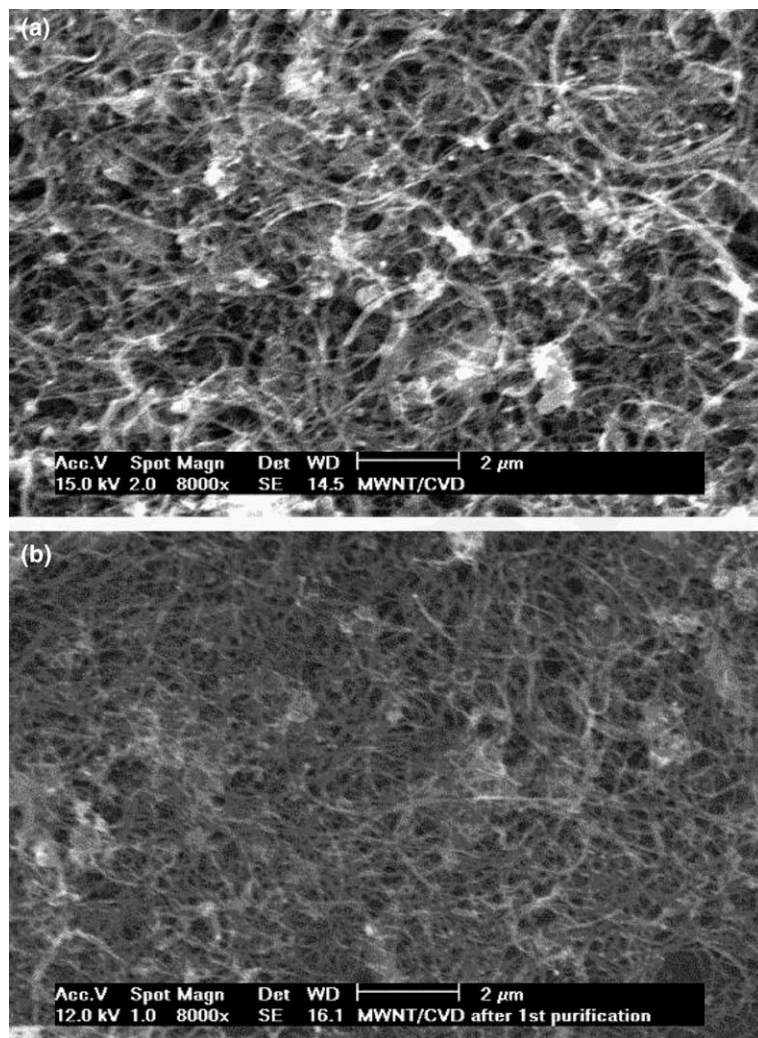


Fig. 3. Low magnification SEM micrographs of (a) unpurified and (b) purified CNTs grown over Fe(III),Co/CaCO₃.

Figs. 4a and b in low and high-magnification, respectively. The latter clearly illustrates that the purification step neither damaged the CNT structure nor generated additional contaminants. The number of catalytic particles, which could be seen as dark spots in Fig. 2c, is considerably reduced as can be compared in Fig. 4a. Moreover, high-resolution observations have shown that the dark spots in the purified sample are not necessarily catalytic particles: only a few dark spots are truly catalytic particles, which were found exclusively in the inner core of MWCNTs. The majority of the

dark spots originate from CNT endings seen with the tube-axis parallel to the beam-direction. Our observation was confirmed by EDX analysis performed by focusing the electron beam onto such dark spots. In Fig. 5 two representative spectra taken from an unpurified and a purified sample are compared; the characteristic peaks for Fe (K_{α} 6.4 eV and K_{β} 7.06 eV) and Co (K_{α} 6.93 eV and K_{β} 7.65 eV) are drastically reduced in the purified sample. Typically we obtained a purity of about 95 wt%.

TGA of purified samples, which was carried out in air, revealed a significant drop of mass at about

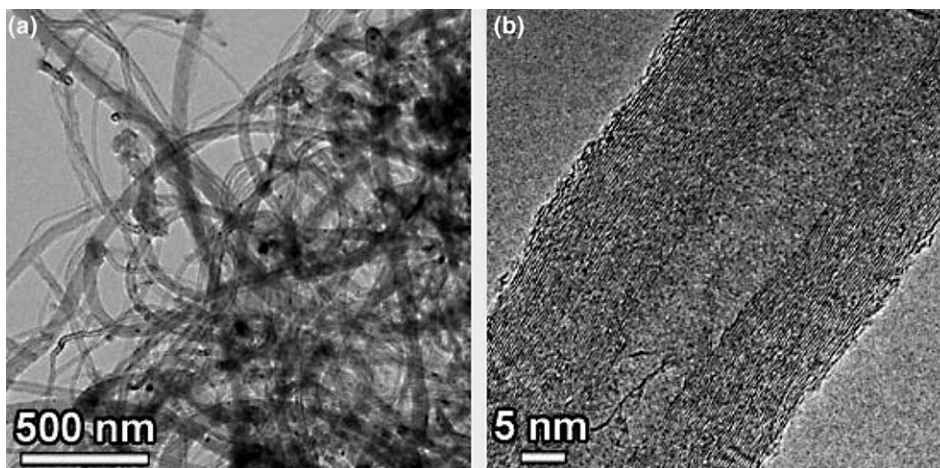


Fig. 4. Low magnification (a) and high-resolution (b) TEM micrographs of CNTs grown over Fe(III),Co/CaCO₃ after purification: catalyst particles and support were dissolved in 30% nitric acid. Most of the dark spots on low magnification image are due to nanotube endings aligned parallel to the electron beam. In the high-resolution image, no amorphous carbon layer is visible on the outer surface of the nanotube.

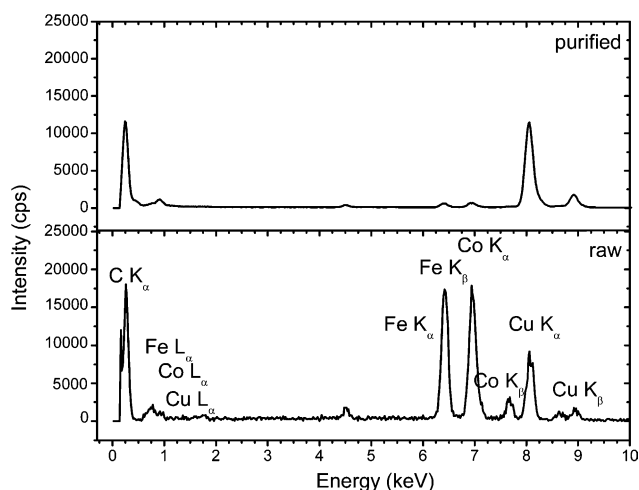


Fig. 5. EDX spectra of unpurified and purified samples. The electron beam was focused onto an area with dark contrast (see Figs. 2c and 4a) where catalysts or support material was suspected. The strong Cu peaks originate from the Cu-grid used as TEM supporting grid.

650 up to 800 °C. This weight loss has to be correlated with the decomposition of MWCNTs via oxidation (inflexion point of TGA curve), as the characteristic combustion temperature of disordered carbon usually emerges at around 400 °C. Consequently, these observations strongly support that the purified MWCNTs are free of contami-

nants or amorphous carbon. In total, 100 mg catalyst approximately resulted in about 70 mg of purified MWCNTs. Our standard fixed-bed flow reactor typically yields approximately 700 mg of purified MWCNTs per day. Using our new rotary-tube oven, mass production of purified CNTs in the scale of 100 g per day can be performed. The

main advantage of the rotary furnace is to realize continuous CVD synthesis of carbon nanotubes instead of the conventional semi continuous operation. The synthesis in the fixed bed flow reactor has to be stopped after certain periods of time in order to charge fresh catalyst portions. Changing catalytic reactor will not affect either activity or selectivity. Operating parameters such as rotation speed of the tube, inclination, catalyst particle size, etc. can modify residence time indeed, however, these variables can be effectively controlled. Results obtained from the fixed bed flow reactor suggest [15,16] that reaction time can be varied in a wide range (5–90 min) without loss of selectivity.

In the last few years, the catalytic method has undergone dramatic improvements (e.g. [10,12]). In particular, recent developments in CVD synthesis of MWCNTs by decomposition of hydrocarbons offer possible routes to the large-scale production of high purity CNTs [21,22]. Nevertheless, purification after the catalytic method involves the separation and the removal of catalyst particles, support material and amorphous nanoparticles from CNTs. Since these materials mostly have to be removed independently by different chemicals, the purification of catalytically prepared CNTs can become a multi-step procedure [20] and one risks additional contamination and/or structural damage of the CNTs after each step. In general, metallic particles can be easily dissolved in diluted mineral acids [23]. The removal of the catalyst support is more problematic: For instance, silicon-containing materials can only be dissolved in hydrofluoric acid. The handling with the latter chemical is rather hazardous, and the waste disposal requires special maintenance even in laboratory scale. The use of aluminium oxide catalyst support somewhat simplifies the purification process since this material is soluble in concentrated alkali solution. However, Nagaraju et al. [24] pointed out that an additional treatment with acidic dissolution would be necessary if the catalyst particles could not be sufficiently dissolved during the first step.

Recent results based on silicagel- or zeolite-supported catalysts made evident that porous materials are excellent supports in catalytic nanotube production [15,16]. However, porous sup-

ports tend to accumulate huge amount of amorphous carbon during the synthesis. With respect to the reaction conditions (especially the temperature) during the catalytic CNT synthesis, acetylene is decomposed in either homogeneous or catalytic reaction. In case of porous support, catalyst particles on outer surfaces proved to be rather selective for CNT formation whereas the inner centers produce amorphous carbon. For elimination of the carbon byproducts, various techniques such as filtration, chromatography and centrifugation were applied [25,26]. Although CNTs could be separated to some extent from carbonaceous particles, a considerable amount of amorphous carbon remained in the purified sample [19]; moreover, the yield of the purified CNTs was generally very low. Oxidation is also an efficient purification method but proceeds on an arbitrary basis and destroys the CNT wall structure. Literature data are not conclusive whether the oxidative etching rate of amorphous material is faster or competitive to that of CNTs. Intuitively one can assume that amorphous carbon is attacked from any direction, whereas CNTs can only be oxidized from the ends [27]. An alternative approach to reduce the amount of amorphous carbon might be the use of aluminium hydroxide support, which was recently suggested [24].

By using CaCO_3 as catalyst support, we can overcome all these difficulties of catalytic CNT production. CaCO_3 is a non-porous material where the formation of amorphous carbon is suppressed during the nanotube growth, and therefore selective formation of CNTs is promoted. Consequently, the subsequent purification can be achieved in one step; both metallic particles and catalyst support can be dissolved in diluted mineral acids (e.g. HNO_3 , HCl). Since CaCO_3 has no pores, no additional residual can be trapped during and after acidic treatment, hence, yielding CNTs with high yield, high purity and less damage of graphitic walls. Moreover, CNT production can be carried out in a simple apparatus at relatively low reaction temperature compared to other techniques, such as arc-discharge and laser ablation. Recently, MgO has been reported to be effective for the growth of high-quality SWCNTs [17,28,29] and MWCNTs [30,31]. Nevertheless,

their purification involves acidic treatments in diluted [17,28,29] or concentrated HCl [32], in boiling concentrated HCl [30] or in 65% HNO₃ [33]. So far our purification method using 30% HNO₃ can be found as one of the mildest acid treatments. An additional advantage of using CaCO₃ as catalyst support is the decomposition of CaCO₃ into CaO and CO₂ at the reaction temperature. Hence, after synthesis only the half of the applied amount of support remains to remove, which simplifies the purification procedure significantly.

One application of these highly pure CNTs is the synthesis of MWCNT-based composites: very recently we demonstrated that CNTs, which were produced and purified in the way described here, could be homogeneously coated with alumina, silica or titania [34]. The most important issue for a homogeneous coverage of CNTs is an effective bonding between CNT surface and precursors, which can only be established when the surface is free of amorphous carbon or other contaminants. Hence, the successful realization of composites clearly demonstrates the high purity of the CNTs obtained using CaCO₃ catalyst support.

In conclusion, our approach of using CaCO₃ results in an efficient selective formation of CNTs in their catalytic growth and enables simple one-step purification without perceivable damage of the CNT structure. We have also shown that the large-scale production (100 g/day) of MWCNTs is possible by using CaCO₃ support in a rotary-tube oven. These results open the door for formation of CNT-based composites and raise hope for a large-scale and low-cost synthesis of CNTs suitable for industrial application.

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References

- [1] S. Iijima, *Nature* 56 (1991) 354.
- [2] C.Y. Moon, Y.S. Kim, E.C. Lee, Y.G. Jin, K.J. Chang, *Phys. Rev. B* 65 (2002) 155401.
- [3] J.A. Steckel, K.D. Jordan, P. Avouris, *J. Phys. Chem. A* 106 (2002) 2572.
- [4] J.N. Coleman, D.F. O'Brien, B. McCarthy, R.C. Barklie, W.J. Blau, *Monatsh. Chem.* 132 (2001) 53.
- [5] J.M. Bonard, T. Stora, J.P. Salvetat, F. Maier, T. Stockli, C. Duschl, L. Forro, W.A. de Heer, A. Chatelain, *Adv. Mater.* 9 (1997) 827.
- [6] F.T. Edelmann, *Angew. Chem.-Int. Edit.* 38 (1999) 1381.
- [7] B. Chen, G. Parker, J. Han, M. Meyyappan, A.M. Cassell, *Chem. Mater.* 14 (2002) 1891.
- [8] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, *Chem. Phys. Lett.* 260 (1996) 471.
- [9] J. Kong, A.M. Cassell, H. Dai, *Chem. Phys. Lett.* 292 (1998) 567.
- [10] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith, R.E. Smalley, *Chem. Phys. Lett.* 313 (1999) 91.
- [11] S. Murayama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* 360 (2002) 229.
- [12] A. Cassell, L. Delzeit, C. Nguyen, R. Stevens, J. Han, M. Meyyappan, *J. Phys. IV* 11 (2001) 401.
- [13] J.M. Bonard, R. Kurt, C. Klinke, *Chem. Phys. Lett.* 343 (2001) 21.
- [14] V. Ivanov, J.B. Nagy, P. Lambin, A. Lucas, X.B. Zhang, X.F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx, J. Van Landuyt, *Chem. Phys. Lett.* 223 (1994) 329.
- [15] K. Hernadi, A. Fonseca, P. Piedigrosso, M. Delvaux, J.B. Nagy, D. Bernaerts, J. Riga, *Catal. Lett.* 48 (1997) 229.
- [16] K. Hernadi, A. Fonseca, J.B. Nagy, D. Bernaerts, A. Fudala, A.A. Lucas, *Zeolites* 17 (1996) 416.
- [17] Q.W. Li, H. Yan, Y. Cheng, J. Zhang, Z.F. Liu, *J. Mater. Chem.* 12 (2002) 1179.
- [18] C. Laurent, A. Peigney, A. Rousset, *J. Mater. Chem.* 8 (1998) 1263.
- [19] K. Hernadi, A. Siska, L. Thien-Nga, L. Forro, I. Kiricsi, *Solid State Ion.* 141 (2001) 203.
- [20] K. Hernadi, A. Fonseca, J.B. Nagy, D. Bernaerts, J. Riga, A. Lucas, *Synth. Metals* 77 (1996) 31.
- [21] V.K. Varadan, J. Xie, *Smart Mater. Struct.* 11 (2002) 728.
- [22] C.J. Lee, S.C. Lyu, H.-W. Kim, C.-Y. Park, C.-W. Yang, *Chem. Phys. Lett.* 359 (2002) 109.
- [23] P.X. Hou, S. Bai, Q.H. Yang, C. Liu, H.M. Cheng, *Carbon* 40 (2002) 81.
- [24] N. Nagaraju, A. Fonseca, Z. Konya, J.B. Nagy, *J. Mol. Cat. A-Chem.* 181 (2002) 57.
- [25] G.S. Duesberg, J. Muster, H.J. Byrne, S. Roth, M. Burghard, *Appl. Phys. A* 69 (1999) 269.
- [26] R. Murphy, J.N. Coleman, M. Cadek, B. McCarthy, M. Bent, A. Drury, R.C. Barklie, W.J. Blau, *J. Phys. Chem. B* 106 (2002) 3087.
- [27] N. Yao, V. Lordi, S.X.C. Ma, *J. Mater. Res.* 13 (1998) 2432.

- [28] J.-F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Konya, A. Fonseca, Ch. Laurent, J.B. Nagy, Chem. Phys. Lett. 316 (2000) 83.
- [29] R.R. Bacsa, Ch. Laurent, A. Peigney, W.S. Bacsa, Th. Vaugien, A. Rousset, Chem. Phys. Lett. 323 (2000) 566.
- [30] Y. Soneda, L. Duclaux, F. Beguin, Carbon 40 (2002) 965.
- [31] I. Willems, Z. Konya, A. Fonseca, J.B. Nagy, Appl. Cat. A. 229 (2002) 229.
- [32] H. Yan, Q. Li, J. Zhang, Z. Liu, Carbon 40 (2002) 2693.
- [33] S. Tang, Z. Zhong, Z. Xiong, L. Sun, L. Liu, J. Lin, Z.X. Shen, K.L. Tan, Chem. Phys. Lett. 350 (2001) 19.
- [34] K. Hernadi, E. Ljubovic, J.W. Seo, L. Forro, Acta Mater. 51 (2003) 1447.