Influence of Fe and Co/Ni on Carbon Arc Plasma and Formation of Fullerenes and Nanotubes

Andrzej Huczko,*,† Hubert Lange,† and Toshiaki Sogabe‡

Department of Chemistry, Warsaw University, Pasteur 1, 02-093 Warsaw, Poland, and Toyo Tanso Co. Ltd., Kagawa 769-1612, Japan

Received: August 4, 2000

Carbon nanostructures (fullerenes and nanotubes) were obtained using the carbon arc technique employing homogeneous carbon−iron and carbon−cobalt−nickel anodes. The influence of these catalysts on the arc plasma was studied by optical emission spectroscopy to determine temperatures and C_2 radical content in the arc zone. The solid products were analyzed by spectrophotometry and mass spectrometry to determine the C_{60} yield and relative mass distributions of the higher fullerenes, respectively. SEM and TEM techniques were used to affirm the presence of carbon nanotubes in the resulting soot product.

Introduction

The arc plasma technique has been known to produce metal nanopowders and composite nanomaterials for years.[1] Specifically, the carbon arc found its application in metallurgy a long time ago,[2] while more recently, carbon nitride, which has received worldwide attention because its characteristics are close to those of diamond, was obtained by the carbon plasma technique.[3] Arc-plasma-produced carbon vapors have also been shown to be the source of fascinating novel nanocarbons—fullerenes[4,5] and nanotubes.[6] The carbon arc co-evaporation of various elements and compounds is known to produce other interesting carbon nanomaterials, e.g., endohedral fullerenes,[7] filled nanotubes,[8] nanotubules,[9] onions,[10] nanoencapsulates,[11] and nanospheres.[12] Some published results regarding these syntheses are, however, inconclusive and even contradictory, mostly due to poor reproducibility and flaws in the experimental techniques. Marked differences in the yields of carbon nanostructures, due to the particular element used in the preparation, have been reported, e.g., in the synthesis of tubules catalyzed by Cu.[13] This is particularly the case in single-wall carbon nanotube (SWNT) formation, where different catalysts and/or process parameters are claimed to be the best. When Fe was used as the catalyst, SWNTs were efficiently grown in a He atmosphere.[14] However, Bethune et al.[15] argued that Fe, Ni, and Ni−Cu mixtures (50:50) do not catalyze the process, while Co does. Iijima and Ichihashi[16] claimed that the synthesis using Fe is successful only when methane is also present in the reactor.

Vaporization of iron by the carbon arc plasma is also known to yield other interesting products. Pradeep et al.[17] obtained the FeC_{60} adduct by contact-arc sublimation of graphite in a partial atmosphere of $Fe(CO)_5$. On the basis of some properties of the obtained adduct, the authors concluded that FeC_{60} was likely an endohedral species, with the Fe atom inside the C_{60} cage. Roth et al.[18] have provided evidence for an externally bound iron−fullerene complex, $FeC_{60}{}^{+}$. This was generated also in the gas phase by a ligand-exchange reaction of $Fe(C_nH_{2n})^+$ ($n = 2-5$) ions with preformed C_{60}. Complexes of iron-containing fullerenes were also obtained in a plasma jet consisting of iron−carbon species combined with a helium flow.[19,20] Some fulleride−iron materials were synthesized by doping fullerides with iron during the thermal decomposition of ferrocene.[21,22]

Knowledge of the basic phenomena involved in the formation of nanocarbons, which is necessary for optimizing large-scale applications, is rather limited,[23] and the plasma zone in such processes is usually considered as a “black box”. Surprisingly, only a few papers of a mostly qualitative character, related to the diagnostics of the carbon plasma environment, have been published so far.[23−26]

The aim of this present study was to investigate the influence of transition metals, introduced into the carbon arc, on the plasma characteristics and the formation of fullerenes and nanotubes. Although the use of catalysts as arc plasma admixtures is not new, quantitative studies of this kind have never been reported. The application of homogeneously doped graphite anodes with a low content of catalyst metals has also helped in this study to avoid drastic changes of the plasma parameters, as is the case with the more commonly used anodes, which are drilled and filled with metals. In fact, the mode of catalyst introduction into the reaction system can distinctly influence the process yield. Thus, a much larger quantity of SWNTs was obtained by Shi et al.[27] by using a Y−Ni alloy composite graphite material as the anode for dc arc discharge, as compared to the yield via a metallic yttrium and nickel catalyst mixture.

During the arcing, optical emission spectroscopy on the arc zone was carried out to determine temperatures and C_2 column densities across the arc section. The arc interior temperature plays an important role in the high-yield synthesis of nanocarbons, e.g., temperature control is very important for nanotube growth.[28] The C_2 radical is only one of the numerous intermediate carbon species that can be quantitatively measured using conventional optical emission spectroscopy.[29−31] This radical is generally accepted[32] to play an important role in the mechanism of fullerene and nanotube formation. Hence, it is of considerable importance to quantitatively study its presence in the reaction zone. The composition of the solid products was also studied by various techniques, and gas-phase speciation of

---

* Corresponding author. E-mail: ahuczko@chem.uw.edu.pl.
† Warsaw University.
‡ Toyo Tanso Co. Ltd.

10.1021/jp002842q CCC: $19.00

TABLE 1: Operating Parameters and C_{60} Fullerene Yield

electrode composition	pressure (kPa)	current (A)	voltage (V)	input power (W)	sublimation rate (mg/s)	C_{60} content (wt %)
C	8	74	19	1406	3.9	10.5
	40	71	23	1633	3.3	7.3
	80	64	29	1856	3.9	4.8
C−Fe	8	79	25	1975	3.3	4.4
	40	70	28	1960	2.9	4.5
	80	71	31	2201	3.6	6.4
C−Co/Ni	8	65	22	1430	4.2	5
	40	76	28	2128	3.6	4.5
	80	78	31	2418	3.3	5

the catalyst in the arc gap was correlated with the metal content in the cathode deposit and soot.

Experimental Details

The reaction system and experimental procedure have been described in more detail elsewhere.[30] Homogeneous graphite electrodes 6 mm in diameter and containing 0.6 at. % of either Fe or a Co−Ni metal mixture were subjected to dc arcing in a He atmosphere under pressures of 8, 40, and 80 kPa. Experiments with pure graphite anodes were also performed for comparison. The arc current was adjusted to maintain similar sublimation rates for the anode (between 3 and 4 mg s^{-1}) for each electrode type. The electrode gap was kept constant (within 1 mm) using an optoelectronic system. The arc burned in a stationary mode, and the spatial distribution of temperatures and C_2 radicals remained undisturbed for the duration of the observations.

The astronomical CCD ST8 camera and coupled monochromator were used for the plasma diagnostics. The C_2 content of the plasma was determined using the self-absorption effect. The self-absorption is distinctly pronounced in the d $^3\Pi_g \rightarrow$ a $^3\Pi_u$ (0−0, 516.5 nm) emission band. The temperature and column density of C_2 (the product of average concentration and column length along a given chord in the arc cross section) were estimated by comparing the experimental spectra with those calculated for various temperatures and column densities of C_2.[31] The temperatures were also estimated from the well-known Boltzmann plots, using some of the sufficiently resolved rotational components of the band. It had been shown earlier[33] that in the case of significant self-absorption, the spectra fitting method and Boltzmann plot lead to temperatures a few hundred degrees higher and lower than the real values, respectively. Therefore, the temperatures reported here were the mean values from the combination of both approaches.

Soot, produced by the arc sublimation of the test anodes, was boiled under reflux in dry toluene prior to C_{60} determination by conventional spectrophotometric measurements at 329 nm. For the identification of the higher fullerenes, we analyzed the soot through the laser desorption TOF MS technique. The morphology of carbon nanostructures was investigated by SEM and HRTEM techniques.

Results and Discussion

The processing variables are presented in Table 1. The presence of the catalysts in the electrode material resulted in higher power input compared to that of pure graphite alone. This is probably due to a higher electrical conductivity of both the electrode material and the plasma itself. Thus, to maintain the desired average anode ablation rate of between 3 and 4 mg s^{-1}, we increased the arc power, e.g., from 1860 W for pure graphite to 2200 W (2400 W) in the presence of Fe (or Co−Ni) at higher pressures when this observation was more pronounced.

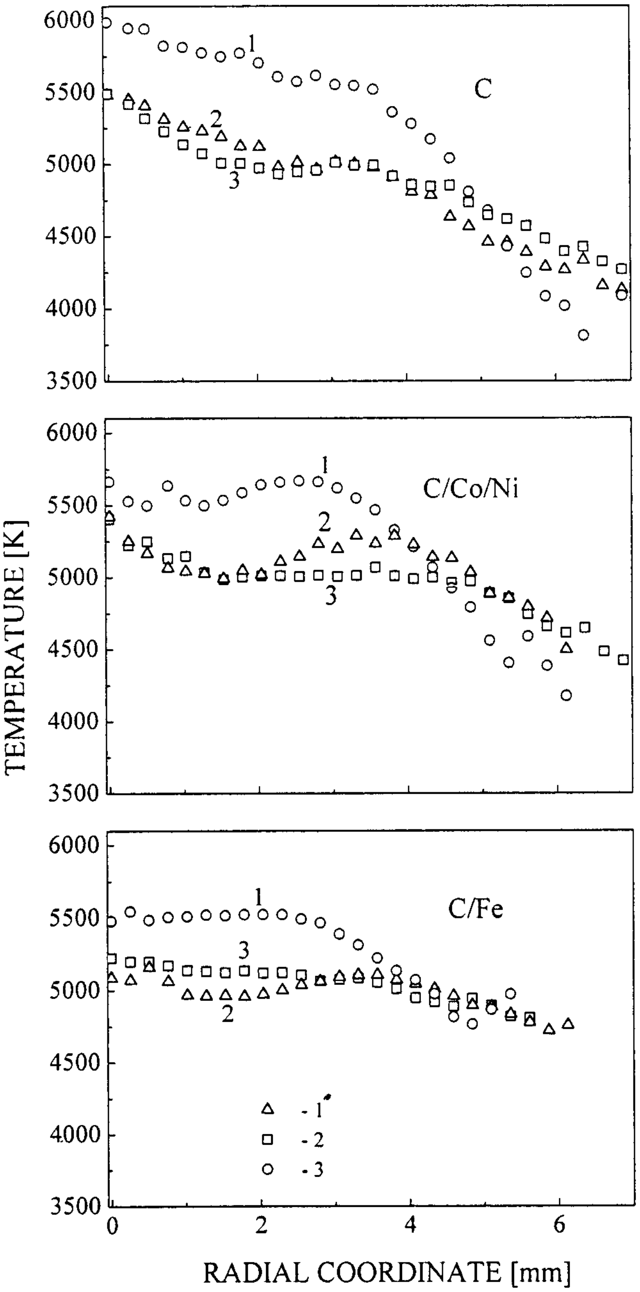

Figure 1. Radial temperature distributions in the arc plasma under pressures of 1−8, 2−40, and 3−80 kPa.

Plasma Temperature and C_2 Content. The results of the spectroscopic measurements of temperatures across a vertical section between the electrodes are presented in Figure 1. The temperatures were derived from non-Abel-inverted spectra. Therefore, the obtained values are to some extent the average temperatures. Obviously, this is the case mainly for the plasma columns along and close to the plasma centerline. Generally, as seen in Figure 1, no great difference exists between the distributions representing the different anode compositions. Nevertheless, in the case of the pure graphite electrode, the radial temperature gradients are slightly higher, probably due to the lower power input (Table 1). The higher temperatures observed at lower pressures (curve 1), independent of the anode composition, are the common feature of the estimated temperature distributions.

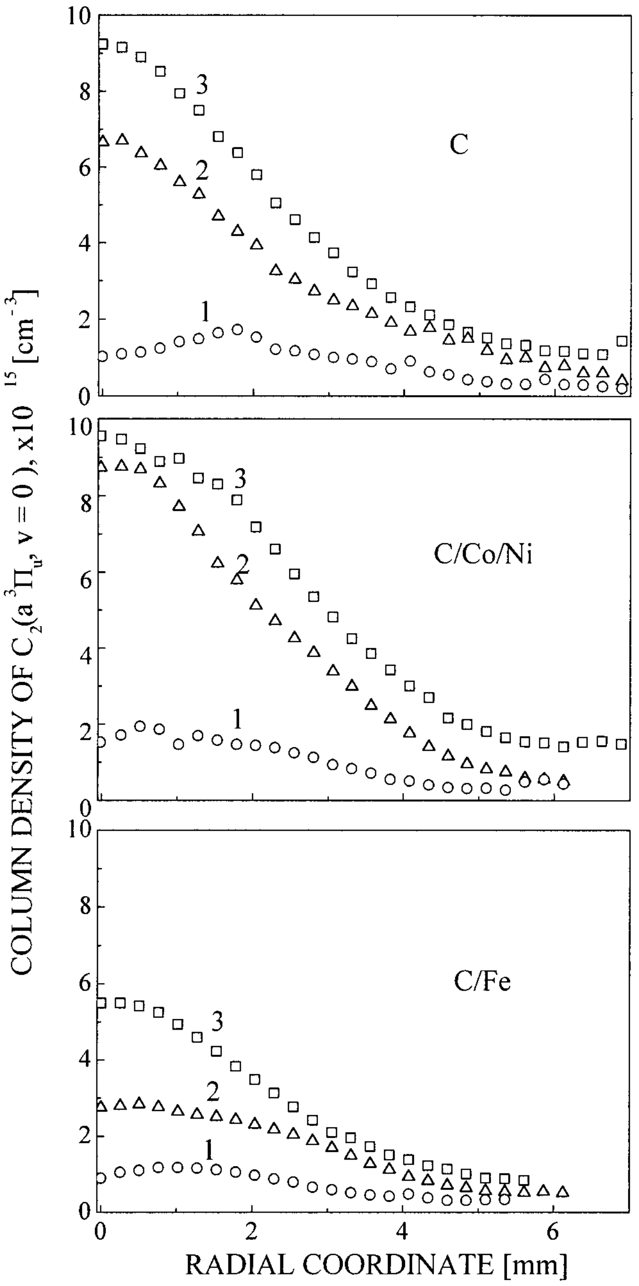

Figure 2. Radial column density distributions of C_2 (a $^3\Pi_u$, $v' = 0$) radicals in the arc plasma under pressures of 1−8, 2−40, and 3−80 kPa.

The column densities for C_2 (a $^3\Pi_u$, $v = 0$) were calculated on the basis of the temperatures and the integrated intensities of the normalized (0,0) vibrational band adjacent to the (1,1) band (516.5−512.9 nm). The results are shown in Figure 2, where it can be seen that He pressure strongly influences the C_2 content in the arc plasma. Despite the similar electrode sublimation rates, more C_2 radicals are generated when the buffer gas pressure in the reactor chamber is higher. Obviously, this increase is due to the lower expansion rates of the carbon species, governed by diffusion, at the higher pressure. Comparing the column density distributions for the different anode compositions, we can see that in the case of the Fe admixture, the C_2 content is lower. This is very intriguing since some physical properties (e.g., ionization potentials) of the elements under consideration are close to one another and none of the catalysts can bond chemically to carbon atoms at plasma temperatures. It must be admitted, however, that because of the small arc gap, the accuracy of the positioning of the target plasma cross section onto the monochromator slit was within ±0.2 mm only. Thus, even a small horizontal displacement can yield results from a different arc cross section than was intended.

Yield of C_{60} and Higher Fullerenes. The final content of the C_{60} fullerene in the collected soot is presented in Table 1 (last column). It shows that at low pressures the presence of the catalysts significantly reduces the yield of C_{60} while at higher pressures the yield is independent of the type of graphite electrode. The use of nonhomogeneous electrodes (drilled and filled with the metals) with much higher Fe content (5.5 at. %) yielded approximately the same (4.5 wt %) amount of C_{60}.[34]

It is known that during the arcing of the graphite, not only C_{60} but also higher, mainly C_{70}, fullerenes are formed. Therefore, the relative mass distributions of higher fullerenes in the solid products for all tests performed were studied by the LD TOF MS technique. The resulting mass spectra, normalized to the C_{60} peak, are presented in Figure 3. The abundance of the higher fullerenes—particularly the so-called "missing fullerenes" C_{72}, C_{74}, and C_{80}—in pure graphite is, as expected, very low.[35] The influence of the catalysts on the formation of those species is evident, with the role of Fe being quite opposite to that of Co/Ni. It is clearly seen that for the anode doped with Fe, the higher fullerene production is distinctly enhanced while for the Co/Ni admixture the effect is opposite, and especially at greater pressures, the generation of the higher fullerenes is nearly totally suppressed. Thus, we can conclude that Fe atoms or clusters may play a catalytic role in generating these, otherwise missing fullerenes.

Carbon Nanotubes. When a dc arc forms on a pure graphite anode, molecular structures known as multiwall carbon nanotubes (MWCNTs) are formed. These nanostructures grow efficiently when the He pressure is great enough (>40 kPa) and the arc gap is kept small during the arcing (<1 mm). The nanotubes can only be found in the core of the cathode deposit and are not detected in other places in the reactor. Coevaporation of carbon and catalyst (mostly metals) in the arc plasma also results in the formation of CNTs (mostly as single-walled structures) at higher pressure, but they are mostly found as a component of the soot. The results of our experiments indicate that even small amounts of the catalysts dramatically change the morphology of the product soot, i.e., the soot is more compact, much less dusty, and more cloth-like in "texture" in comparison to the soot resulting from the sublimation of pure graphite. A weblike product was often found in the discharge chamber. Such webs have been observed already by researchers.[28] The soot collected from the reactor walls and the weblike product were separately analyzed by SEM and TEM. Examples of the electron microscopy images of soot products obtained at low- and high-pressure conditions are shown in Figure 4. The most interesting feature of the soot is the presence of elongated nanostructures, with single-walled nanotubes clearly visible. Some of these nanotubes were covered with a layer of amorphous carbon. In the Fe catalyst, the carbon nanotubules were found mostly in the weblike material surrounding the cathode deposit, while for the Co−Ni catalyst, the comparable nanostructures were found in both the chamber-deposited soot and the webs. However, significant amounts of the nanotube bundles up to several nanometers thick were found only in the webs. The chamber soot contained high concentrations of narrow nanotubes, together with clustered particles of amorphous carbon and catalyst accretions. The catalyst particles were also present in the webs. In contrast to an earlier report,[36] we have not found carbon nanotubes in the cathode "collaret" material.

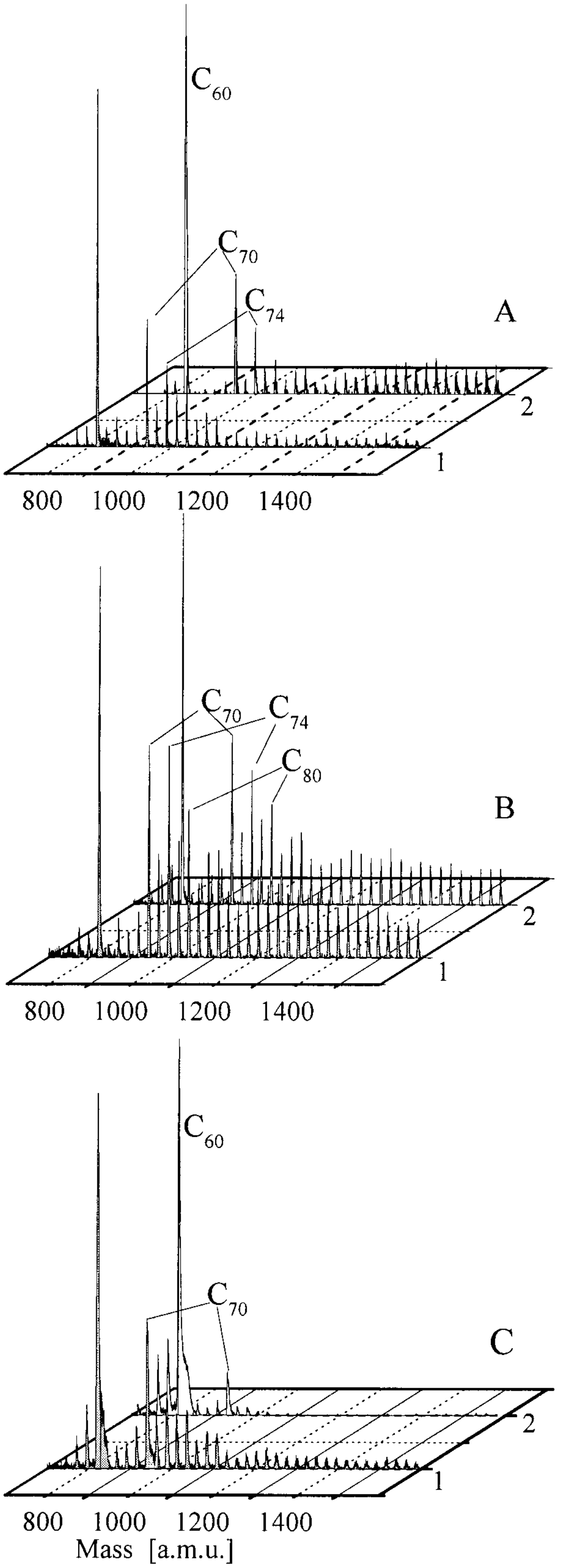

Figure 3. MS of soot produced under pressures of 1−8 and 3−80 kPa. Anode composition: (A) C, (B) C−Fe, and (C) C−Co/Ni.

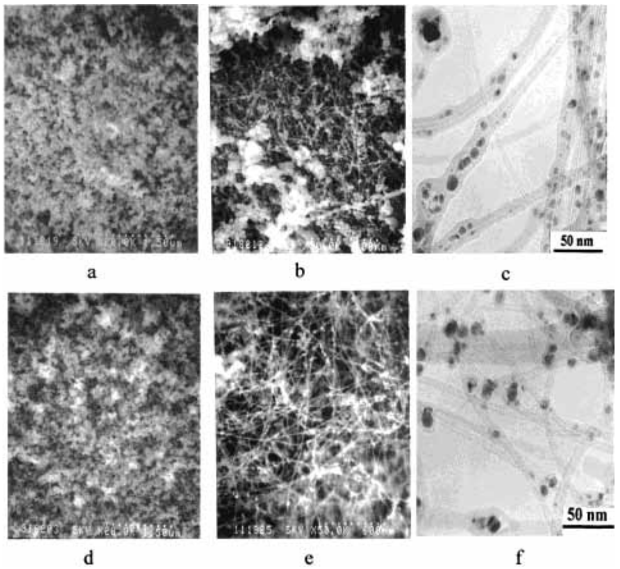

Figure 4. SEM (a, b, d, and e) and TEM (c and f) images of webs and soot containing various amounts of nanotubes and irregular clusters of spherulitic amorphous carbon. C−Fe: (a) web (8 kPa), (b) web (80 kPa). C−Co/Ni: (d) reactor soot (8 kPa), (e) web (80 kPa). C−Fe: (c) web (80 kPa). C−Co/Ni: (f) web (80 kPa).

Wet chemical analysis of the Fe content among the products arising from arc sublimation of heterogeneous anodes made with a high Fe content[34] has shown a highly nonuniform distribution of this catalyst. Fe concentrations of 8.2, 1.3 and 0.2 wt % were found in the reactor soot, the cathode deposit "core", and the turbostratic graphite surrounding this core, respectively. Such a varying distribution is obviously caused by the high-temperature environment (plasma, ∼5000 K; cathode surface, >3200 K) preventing the condensation of the iron vapor. Thus, in the case of the homogeneous electrodes, an explanation is proposed to account for the facts that SWNTs do not grow in the cathode products and that the metal-vapor-catalyzed reactions only occur in the quenching zone of the reactor.

Acknowledgment. The work was supported by the Committee for Scientific Research through the Department of Chemistry, Warsaw University, by Grant 3 T09A 058 16. The authors also thank Dr. P. Lanigan, Dép, génie chimique, University de Sherbrooke, Sherbrooke, Canada, for his comments on and corrections to the text.

References and Notes

(1) Fauchais, P.; Vardelle, A.; Denoirjean, A. *Surf. Coat. Technol.* **1997**, *97*, 66.

(2) Stenkrist, S.-E.; Bowman, B. In *Plasma Technology in Metallurgical Processing*; Feinman, J., Ed.; Iron and Steel Society, Inc., 1987; Chapter 8B.

(3) Meng, X. Q.; Zhang, Z. H.; Guo, H. X.; Li, A. G.; Fan, X. J. *Solid State Commun.* **1998**, *207*, 75.

(4) Kroto, H. W.; Heath, R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(5) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1991**, *354*, 54.

(6) Iijima, S. *Nature* **1991**, *354*, 54.

(7) Braun, T. *Models Chem.* **1995**, *132*, 245.

(8) Maser, W. K.; Lambert, J. M.; Ajayan, P. M.; Stephan, O.; Bernier, P. *Synth. Met.* **1996**, *77*, 243.

(9) Setlur, A. A.; Lauerhaas, J. M.; Dai, J. Y.; Chang, R. P. H. *Appl. Phys. Lett.* **1996**, *69*, 345.

(10) Banhart, F.; Redlich, Ph.; Ajayan, P. M. *Chem. Phys. Lett.* **1998**, *292*, 554.

(11) Saito, Y.; Nishikubo, K.; Kawabata, K.; Matsumoto, T. *J. Appl. Phys.* **1996**, *80*, 3062.

(12) Obraztsova, E. D.; Bonard, J.-M.; Kuznetsov, V. L. *International Winterschool on Electronic Properties of Novel Materials*; Kirchberg, Austria, 1998; American Institute of Physics: Woodbury, NY, 1998; p 132.

(13) Botton, G. A.; Burnell, G.; Humphreys, C. J.; Yadav, T.; Withers, J. C. *J. Phys. Chem. Solids* **1997**, *58*, 1091.

(14) Cassel, A. M.; Scrivens, W. A.; Tour, J. M. *Chem. Mater.* **1996**, *8*, 1545.

(15) Bethune, D. S.; Kiang, C. H.; De Vries, M. S.; German, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(16) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.

(17) Pradeep, T.; Kulkarni, G. U.; Kannan, K. R.; Row, T. N.; Guru; Rao, C. N. R. *J. Am. Chem. Soc.* **1992**, *114*, 2272.

(18) Roth, L. M.; Huang, Y.; Schwedler, J. T.; Cassady, C. J.; Ben-Amotz, D.; Kahr, B.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 6298.

(19) Churilov, G. N.; Bayukov, O. A.; Petrakovskaya, E. A.; Korets, A. Ya.; Isakova, W. G.; Titarenko, Ya. N. *Zh. Tekh. Fiz.* **1997**, *67*, 142.

(20) Ovchinnikov, S. G.; Churilov, G. N.; Isakova, V. G.; Churilova, Ya. N.; Koretz, A. Ya.; Savchenko, A. A.; Fefelova, V. V. *International Winterschool on Electronic Properties of Novel Materials;* Kirchberg, Austria, 1998; American Institute of Physics: Woodbury, NY 1998; p 227.

(21) Byszewski, P.; Kucharski, Z.; Suwalski, J. *Proceedings of the International Winterschool on Fullerenes and Fullerene Nanostructures*; Kuzmany, H., Ed.; Kirchberg, Austria, 1994; World Scientific, River Edge, NJ, 1994; p 82.

(22) Byszewski, P.; Kucharski, Z. *Fullerene Sci. Technol.* **1997**, *5*, 97.

(23) Setlur, A. A.; Lauerhaas, J. M.; Dai, J. Y.; Chang, R. P. H. *Electron. Soc. Proc.* , **1998**, *98* (8), 897.

(24) Afanas'ev, D. V.; Bogdanov, A. A.; Dyuzhev, G. A.; Kruglikov, A. A. *Mol. Mater.* **1996**, *7*, 93.

(25) Belz, T.; Find, J.; Herein, D.; Pfänder, N.; Rûhle, T.; Werner, H.; Wohlers, M.; Schlögel, R. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 712.

(26) Arepalli, S.; Scott, C. D. *Chem. Phys. Lett.* **1999**, *302*, 139.

(27) Shi, Z.; Lian, Y.; Zhou, X.; Gu, Z.; Zhang, Y.; Iijima, S.; Zhou, L.; Yue, K.; Zhang, S. *Carbon* **1999**, *37*, 1449.

(28) Takizawa, M.; Bandow, S.; Torii, T.; Iijima, S. *Chem. Phys. Lett*. **1999**, *302*, 148.

(29) Lange, H.; Byszewski, P.; Kowalska, E.; Radomska, J.; Huczko, A.; Kucharski, Z. *Carbon* **1998**, *37*, 1159.

(30) Huczko, A.; Lange, H.; Byszewski, P.; Poplawska, M.; Starski, A. *J. Phys. Chem. A* **1997**, *101*, 1267.

(31) Lange, H.; Saidane, K.; Razafinimanana, M.; Gleizes, A. *J. Phys. D: Appl. Phys*. **1999**, *32*, 1024.

(32) Osawa, E.; Yoshida, M.; Ueno, H.; Sage, S.-I.; Yoshida, E. *Fullerene Sci. Technol*. **1999**, *7*, 239.

(33) Lange, H. *Symp. Proc. − 14th Int. Symp. Plasma Chem., 14th Praha* **1999**, *1*, 221.

(34) Lange, H.; Huczko, A.; Noworyta, K.; Byszewski, P. *Czech. J. Phys.* **1999**, *49*, 933.

(35) Wan T. S. M.; Zhang H.-W.; Nakane, T.; Xu, Z.; Inakuma, M.; Shinohara, H.; Kobayashi K.; Nagase S. *J. Am. Chem. Soc.* **1998**, *120*, 6806.

(36) Journet C.; Bernier P. *Appl. Phys.* **1998**, *A67*, 1.