lar sieve membrane seems to be very sensitive to some preparation factor(s) other than total carbon mass and application of the polymer onto the support. Further study is needed to isolate and better control these factors.

Acknowledgements

Funding for this research was provided by the DuPont Company, the State of Delaware Research Partnership and the Department of Energy, Office of Basic Energy Sciences. Special thanks goes to Mr. Joseph Nestlerode, Central Research and Development, DuPont Experimental Station for membrane fabrication and testing.

References

[1] Armor JN. J Membr Sci 1998;147:217.
[2] Harold MP, Lee C. Chem Eng Sci 1997;52:1923.
[3] Keizer K, Verweij H. Chemtech 1996;26:37.
[4] Armor JN. Catal Today 1995;25:199.
[5] Acharya M, Raich BA, Foley HC, Harold MP, Lerou JJ. Ind Eng Chem Res 1997;8:2924.
[6] Chen YD, Yang RT. Ind Eng Chem Res 1994;93:3146.
[7] Rao MB, Sircar S. J Membr Sci 1996;110:10.
[8] Geiszler VC, Koros WJ. Ind Eng Chem Res 1996;35:2999.
[9] Foley HC. Microporous Mater 1995;4:407.
[10] Foley HC, Kane MS, Goellner JF. In: Pinnavaia TJ, Thorpe MF, editors, Access in nanoporous materials, New York: Plenum, 1995.
[11] Shiflett MB, Pedrick JF, McLean SR, Subramoney S, Foley HC. Adv Mater 2000;12:21.
[12] Mariwala RK, Foley HC. Ind Eng Chem Res 1994;33:607.
[13] Kane MS, Goellner JF, Foley HC, DiFrancesco R, Billinge SJ, Allard LF. Chem Mater 1996;8:2159.
[14] Petkov V, DiFrancesco RG, Billinge SJ, Acharya M, Foley HC. Phil Mag 1999;79:1519.
[15] Acharya M, Strano MS, Mathews JP, Billinge SJ, Petkov V, Subramoney S, Foley HC. Phil Mag 1999;79:1499.
[16] Koresh JE, Soffer A. Sep Sci Technol 1987;22:973.
[17] Koresh JE, Soffer A. J Chem Soc Farad Trans 1986;82:2057.
[18] Acharya M, Foley HC. J Membr Sci 1999;161:1.
[19] Shiflett MB, Foley HC. Science 1999;285:1902.
[20] Shiflett MB, Foley HC, Yokozeki A. AIChE J (2000) accepted.
[21] Shiflett MB, Foley HC. J Membr Sci 2000;179:275.

Formation of a novel carbon microstructure using laser atomization: carbon nanocurls

R. Houriet[a,*], R. Vacassy[a], H. Hofmann[a], Y. Von Kaenel[b], H. Hofmeister[c]

[a]*Laboratoire de Technologie des Poudres, EPFL, CH-1015 Lausanne, Switzerland*
[b]*Laboratoire de Métallurgie Physique, EPFL, CH-1015 Lausanne, Switzerland*
[c]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

Received 23 October 2000; accepted 20 February 2001

Keywords: A. Vapor grown carbon; B. Laser irradiation; D. Microstructure; Chemical structure

A kind of revolution in carbon science and technology has occurred over the last 20 years or so in the use of various carbon materials which has spread into several technological developments, such as carbon fibers, diamond-like materials and others. From a fundamental point of view, carbon has indeed generated a wealth of basic research, both experimental and theoretical, due to the discovery of several new structures such as fullerenes, nanotubes and related structures. For recent reviews, see Refs. [1,2]. Carbon materials with nanometre-scale structure have shown promising use as building blocks for the future generation of small electronic devices. The recent discovery of carbon nanotubes has opened new perspectives in microelectronics and the search for new possible technological applications is being fruitfully investigated.

Here we report on the application of the Lina-Spark™ atomizer, LSA, to the formation of new carbon structures, the so-called carbon nanocurls. Recent experiments have shown that LSA is a suitable method for preparing particular three-dimensional thin films with interconnected particles forming a web-like structure that have at least 95% porosity [3]. We thus expect that the atomization of carbon material can provide such unusual microstructures.

The experimental LSA set-up is shown in Fig. 1. Briefly, it consists of a pulsed Nd-YAG laser, 1.06 μm, which is focused on the target material. The lens mount is

*Corresponding author. Tel.: +41-21-693-4908; fax: +41-21-693-3089.
E-mail address: raymond.houriet@epfl.ch (R. Houriet).

0008-6223/01/$ – see front matter
PII: S0008-6223(01)00087-2

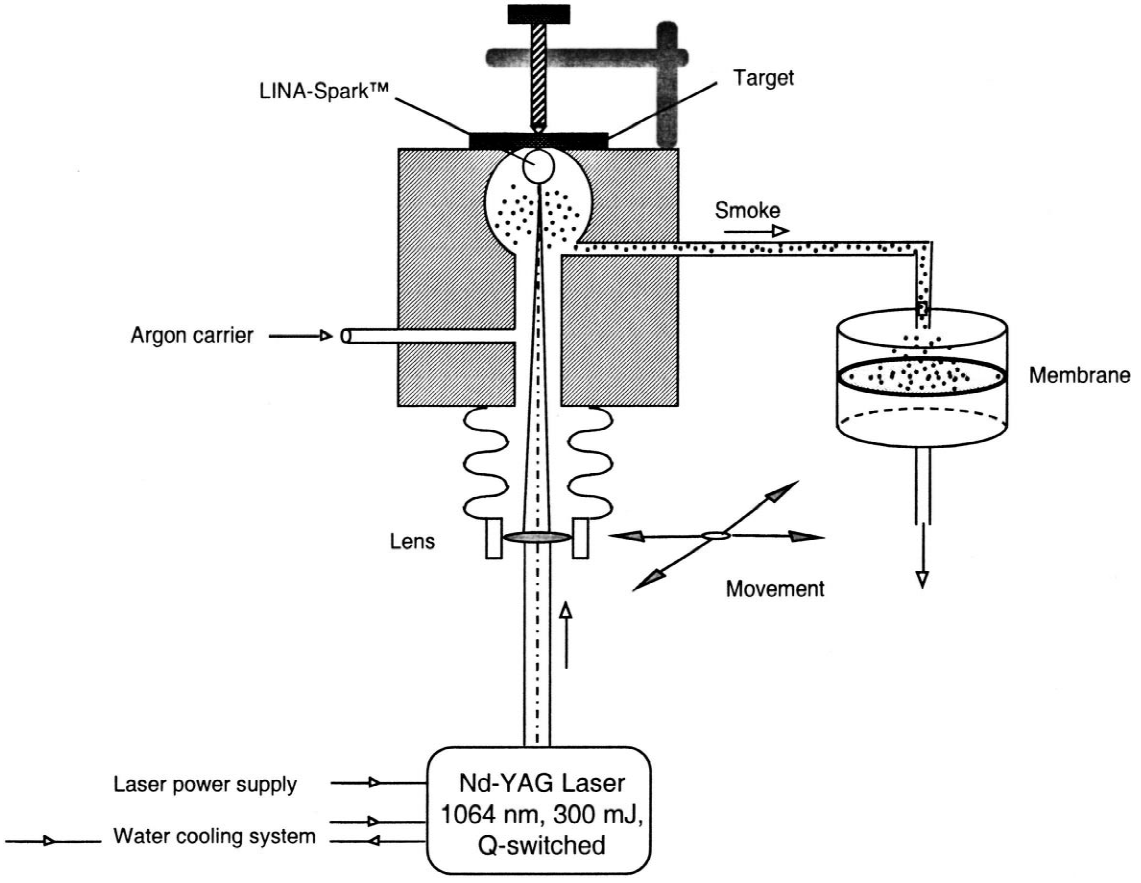

Fig. 1. Laser spark atomizer, LSA, experimental layout.

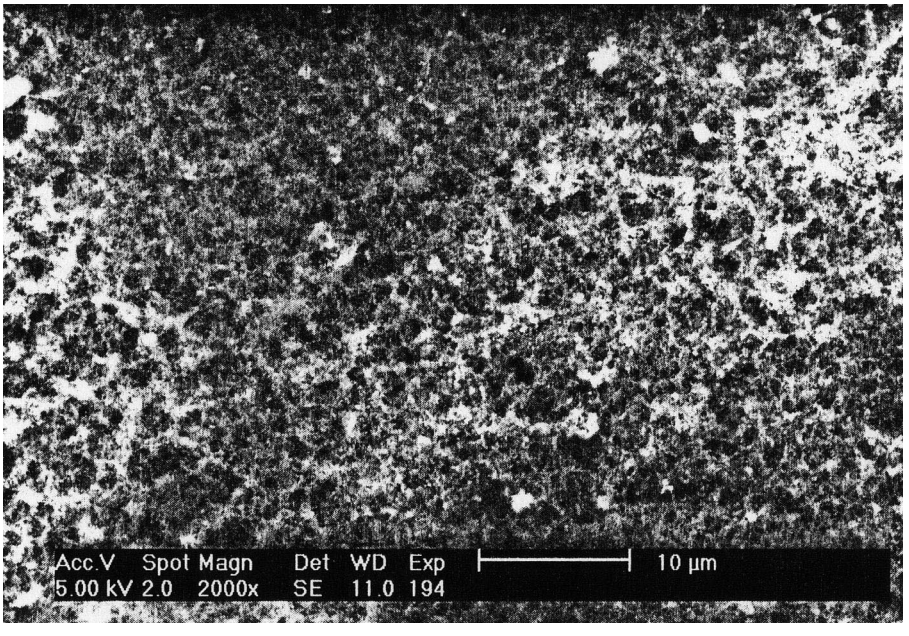

Fig. 2. SEM micrograph of a carbon film formed by LSA. These coatings consist of nanoparticulate materials piled up in a tridimensional mesoporous network forming a web-like structure.

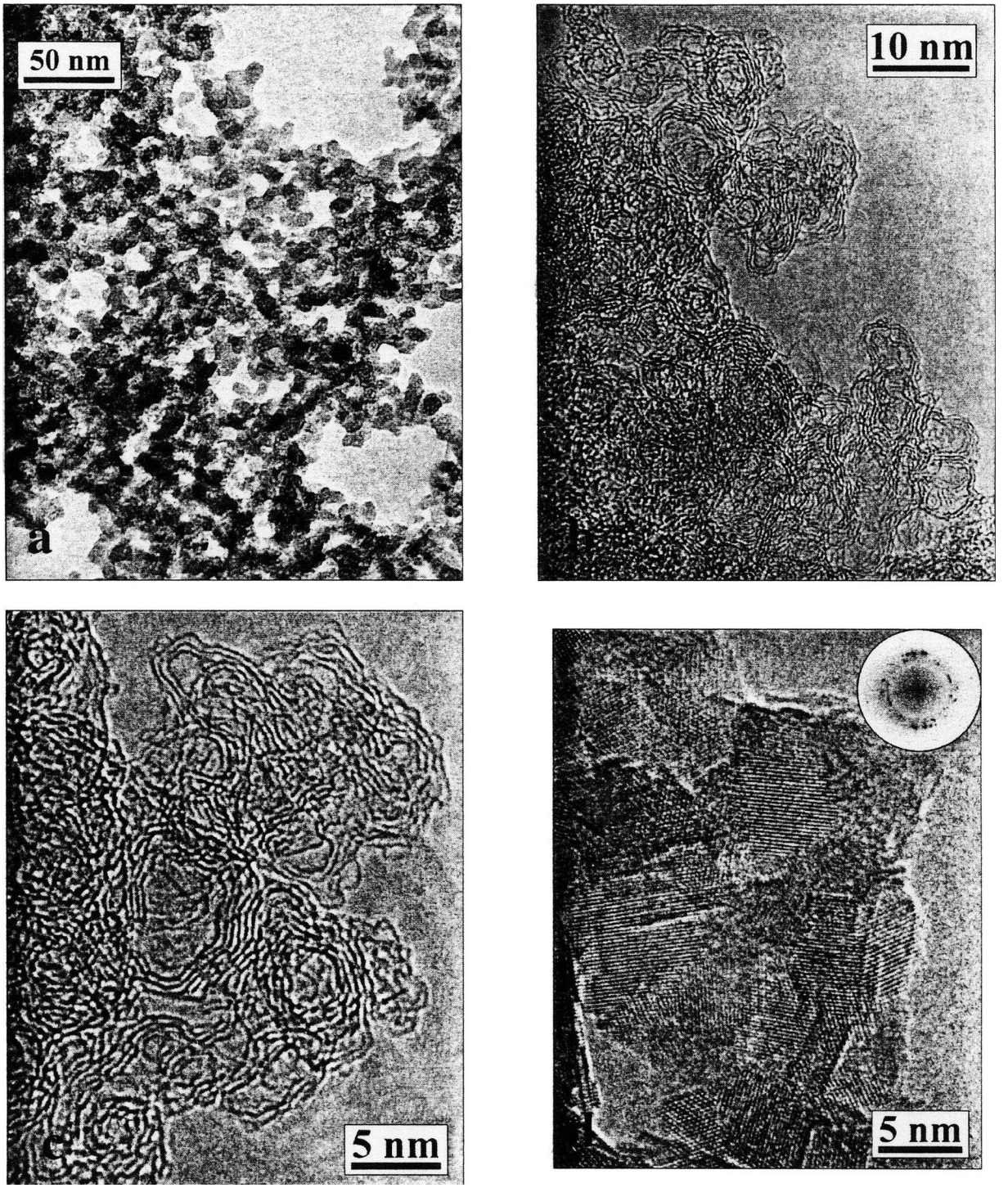

Fig. 3. HRTEM micrographs of the carbon film formed by LSA showing the particulate appearance of the web (a), tangled, curled tubules and globules of the web (b), nanocurls at high magnification (c), and some special nanocrystalline regions of the web (d).

moved so that the laser beam describes a circle on the target, thus avoiding the formation of a crater. The experiment runs under atmospheric pressure of argon with a flow rate around 1 l/min. The evaporation of material occurs from local heating due to the formation of a microplasma. Downstream, the evolved particles eventually condense, agglomerate and solidify, before reaching a membrane where collection of the particles occurs [4]. On arrival onto the membrane which is typically an alumina membrane (Anodisc from Whatman with 20 nm average pore size), the particles pile up to form a fractal three-dimensional network at a rate of about 1 mg/min. The microstructure of the resulting mesoporous thin film can be influenced by the argon flow rate as recently shown [4].

For the present experiments, we used pyrolytic graphite as target material and an argon flow rate of 0.6 l/min.

The films were examined first by infra-red spectroscopy, FTIR, and micro-X-ray fluorescence, XRF, in order to check the chemical purity of the films. Since no significant amount of impurities could be detected, we are certain that our films are at least 99% pure. In particular, the infra-red spectra showed no C–H absorption bands, neither were aromatic C=C absorptions observed.

The microstructure was examined with both scanning electron microscopy, SEM, and high resolution transmission electron microscopy, HRTEM. For HRTEM, the particulate films were dispersed in propanol and transferred to copper microgrids coated by holey carbon films. Electron micrographs were recorded under optimum contrast conditions at a JEM 4000 EX operating at 400 kV. Only regions of the specimen where the particle network was bridging over holes of the supporting film yielded images of good quality. The Raman spectra were measured using a Dilor XY800 spectrometer and an argon ion laser line at 514 nm.

The overall features of the carbon films produced by the LSA method are quite similar to those observed previously, i.e. as seen in Fig. 2 a quite homogeneous film is formed with the typical highly mesoporous structure, analogous to those obtained from targets made out of refractory materials [3,4]. Again, a thick film can be produced, in this case thickness was about 18 μm as measured on an SEM cross section. The SEM micrograph shown in Fig. 2 reveals a web-like structure with components loosely interwoven into one another. More details of the microstructure are found in the HRTEM micrographs. From Fig. 3a the particulate appearance of the web may be recognized with primary particles of 8.4 nm mean size forming the yarn. At the next level of structure shown in Fig. 3b, this web is found to consist of tangled and curled tubules and globules. It is this appearance of the material that led us to the designation ‘nanocurls’. At somewhat higher magnification, as given in Fig. 3c, it can be seen that the nanocurls are composed of heavily curved graphitic layers. These features are clearly different from those of nanotubes since they do not have a straight-

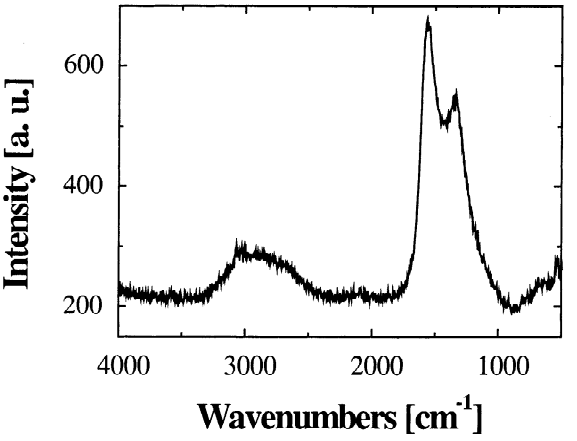

Fig. 4. Raman spectrum of the carbon film produced by LSA.

forward geometry. They are also quite distinct from so-called onion-like structures [1]. Some regions of the web are found to consist of interconnected graphite nanocrystallites that can be seen in Fig. 3d. The diffractogram in the circular inset indicates their random orientation. The lattice fringes here mainly correspond to {10.0} and {10.1} planes having 0.213 and 0.203 nm spacing, respectively, whereas the curved graphitic layers of Fig. 3c almost exclusively exhibit {00.2} fringes of around 0.335 nm spacing.

The Raman spectrum of the carbon film produced by LSA is shown in Fig. 4. The spectrum exhibits two major lines centered about 1342 and 1564 cm^{-1}. Whereas the former can clearly be attributed to nanocrystalline graphite, the latter corresponds to the 1580 cm^{-1} line usually found for graphite, slightly red-shifted due to size effect, see Ref. [1]. The composite peak structure in this area was deconvoluted using a peak fitting procedure showing the presence of a small residue, which indicates that the presence of small quantities of sp^2 and sp^3 amorphous carbon cannot be entirely ruled out. The low intensity structureless line at 2950 ± 100 cm^{-1} is probably a superposition of graphite second-order and combination bands.

In summary, a novel carbon microstructure (nanocurls) has been obtained using laser atomization. The influence of the operating parameters on the nanocurl microstructure are now under investigation.

Exploring the novel electronic, chemical and structural properties of nanocurls might open new perspectives in microelectronics for applications such as molecular switches, molecular wires and even as mesoscopic metal-semiconductor devices [5].

Acknowledgements

Financial support of the Fonds National Suisse is gratefully acknowledged.

References

[1] Dresselhaus MS, Dresselhaus G, Eklund PC. Science of fullerenes and carbon nanotubes, San Diego: Academic Press, 1996.
[2] Dresselhaus MS. Future directions in carbon science. Annu Rev Mater Sci 1997;27:1–34.
[3] Houriet R, Vacassy R, Hofmann H, Vogel W. Thin film growth using ablation of ceramics with a Lina-Spark™ atomizer. Mater Res Soc Symp Proc 1998;526:117–22.
[4] Houriet R, Vacassy R, Hofmann H. Synthesis of powders and films using a new laser ablation technique. Nanostruct Mater 1999;11(8):1155–63.
[5] Tanaka K, Yamabe T, Fukui K, editors, The science and technology of carbon nanotubes, Amsterdam: Elsevier, 1999.

Small diameter carbon nanotubes synthesized in an arc-discharge

Yubao Li*, Sishen Xie, Weiya Zhou, Dongsheng Tang, Zhuqin Liu, Xiaoping Zou, Gang Wang

Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, China

Received 29 January 2001; accepted 26 February 2001

Keywords: A. Carbon nanotubes; B. Arc discharge; C. Transmission electron microscopy

Carbon nanotubes have attracted much attention owing to their special properties and intriguing applications in many fields. It has been demonstrated that they possess excellent mechanical properties and have interesting electric transport behavior. Carbon nanotubes are regarded as an ideal one-dimensional quantum wires and can be either metallic or semiconducting, depending on their diameter and helicity [1]. Therefore, to synthesize carbon nanotubes with well-defined structures is of great importance to their actual applications and the related fundamental research. But, as estimated by Blase et al. [2], small diameter carbon nanotubes tend to be metallic owing to the sufficiently strong σ^*–π^* hybridization effects which dramatically change the band structure. So far, many researchers have tried to synthesize the smallest nanotubes, and the nanotubes with diameters of 0.7 [3], 0.5 [4] and 0.4 nm [5] have been observed. In a previous letter, we reported the synthesis of nanographite ribbons by utilizing a SiC rod as the anode to an arc-discharge in hydrogen [6]. When choosing helium gas as the discharge atmosphere, we found that a similar arc-discharge process led to the creation of small diameter carbon nanotubes in mass.

The experiments were carried out in a normal DC arc-discharge apparatus. A SiC rod (7.5 mm in diameter) containing iron impurity acted as the anode and a graphite plate as the cathode. Full details have been published earlier [6]. Before the discharge, 15 kPa pure helium gas was sealed in the chamber and 30 A (35 V) DC electric current was supplied. The discharge process was maintained for 5 min. After the discharge, a column-like deposit had formed on the cathode and the tip of the SiC rod turned black in color. The cathode deposit was directly observed by a scanning electron microscope, and the black powders in its core as well as the black powders left at the tip of anode were dispersed on some microgrids and also checked in a transmission electron microscope.

The black core of cathode deposit is composed of lots of long and straight nanofibers and some nanoparticles. Its SEM image (Fig. 1) shows a typical morphology of a cathode deposit formed in a normal carbon-arc process to

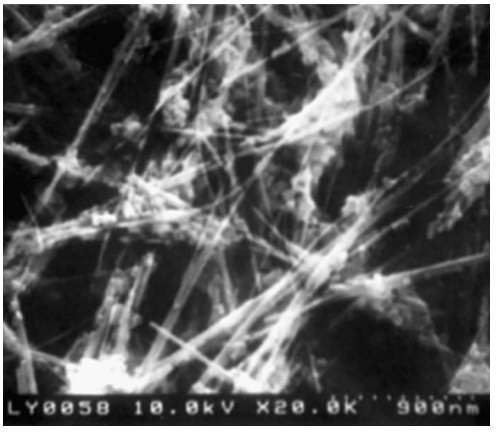

Fig. 1. SEM image of the cathode deposit core.

*Corresponding author. Fax: +86-10-8264-9531.
E-mail address: yubaoli@aphy.iphy.ac.cn (Y. Li).

0008-6223/01/$ – see front matter
PII: S0008-6223(01)00066-5