

Implementation of an Electric Field (AC and DC) for the Growth of Carbon Filaments via Reaction under Autogenic Pressure at Elevated Temperatures of Mesitylene without Catalyst or Solvent

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The electric-field-directed growth of carbon filaments by reactions under autogenic pressure at elevated temperatures (RAPET) of mesitylene without a catalyst, a support, or a solvent is demonstrated. The thermal dissociation of mesitylene at 700 °C in a closed Swagelok cell under air atmosphere in a zero-applied electric field exhibits no preferred orientation and forms $2.5 \pm 0.05 \mu\text{m}$ spherical carbon bodies. In contrast, a one-dimensional growth of carbon filaments is produced with the application of constant direct currents [DC] in the range of 1.5–5 A. The application of an AC [1.5–5 A] current yielded, in addition to the straight filaments, peculiar carbon filaments with sharp edges, zigzag-, dipod-, and tripod-like carbon microstructures, and other morphologies. A plausible mechanism is proposed for the growth of carbon filaments under the implementation of AC or DC electric fields.

Introduction

The electronic structures between diamond (sp^3 -carbon) and graphite (sp^2 -carbon) are different, although both of them are allotropes of elemental carbon; that is, the former is a typical insulator with a large energy gap, while the latter is semi-metallic. In most cases of disordered carbons that are defined as sp^2/sp^3 mixed carbon, the increase in the sp^2 -carbon ratio tends to establish the graphitic structure, which favors the itinerant electron character as confirmed by high conductivity and large diamagnetism.¹ Carbon scientists throughout the world have been attracted to the study of the structure, texture, and diversity of various carbon materials due to their wide range of application in nano-devices,² energy storage,³ separation technologies,⁴ and lubricants. Carbon nanotubes, spheres, beads, onions, glassy carbon, and pyrolytic carbon have all been synthesized via very different processes. All carbon materials are formed from different precursors, and when heated to about 1300–1500 °C under reduced pressures they form hexagonal layers of carbon atoms.⁵ Each carbon material has a different way of aggregating upon the cooling of these hexagonal layers, which leads to the formation of various textures.

Herein, we highlight a few reports where an electric field is employed for the growth of carbon nanotubes/fibers. Electrical transport data in disordered forms of carbon were recently reviewed by Godet and compared to the bandtail hopping characteristics obtained from a modeling of phonon-assisted tunneling within an exponential density of state distribution.⁶ Using electric field control, the high-rate flame synthesis of vertically aligned carbon nanotubes on a Ni-based catalytic support was carried out by Merchan et al.⁷ Aligned, single-walled carbon nanotubes are grown onto the surfaces of SiO_2/Si substrates in electric fields established across patterned metal electrodes.⁸ The application of alternating electric fields for the alignment and network formation of carbon nanofibers in an epoxy resin dispersion during curing is also discussed.⁹ The electric-field-assisted assembly of single walled carbon nanotubes (SWCNTs) on lithographically patterned electrodes has been studied using both DC and AC electric fields. The nanotube alignment is strongly dependent on the magnitude and the frequency of the applied electric field. An improved carbon nanotube (CNT) orientation is achieved with an AC electric field of high frequency due to alternating force exerted rapidly on field-induced dipoles of the nanotubes, which orientate nearly at right angles to the metal electrodes.¹⁰

The RAPET (reactions under autogenic pressure at elevated temperature) process has recently been developed and

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- (1) Akai, K. T.; Oga, M.; Enoki, T.; Taomoto, A. *Diamond Relat. Mater.* **2004**, *13*, 1469–1473.
- (2) Collins, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100.
- (3) Che, G. L.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346.
- (4) Shiflett, M. B.; Foley, H. C. *Science* **1999**, *285*, 1902.
- (5) Inagaki, M. *Solid State Ionics* **1996**, *86–88*, 833.

- (6) Godet, C. *Diamond Relat. Mater.* **2003**, *12*, 159–165.

- (7) Merchan-Merchan, W.; Saveliev, A. V.; Kennedy L. A. *Carbon* **2004**, *42*, 599–608.

- (8) Ural, A. L.; Dai, Y. H. *Appl. Phys. Lett.* **2002**, *81*, 3464–66.

- (9) Cavaille, J.-Y.; Bauhofer, W. *Compos. Sci. Technol.* **2003**, *63*, 1835–1841.

- (10) Senthil Kumar, M.; Kim, T. H.; Lee, S. H.; Song, S. M.; Yang, J. W.; Nahm, K. S.; Suh, E.-K. *Chem. Phys. Lett.* **2004**, *383*, 235–239.

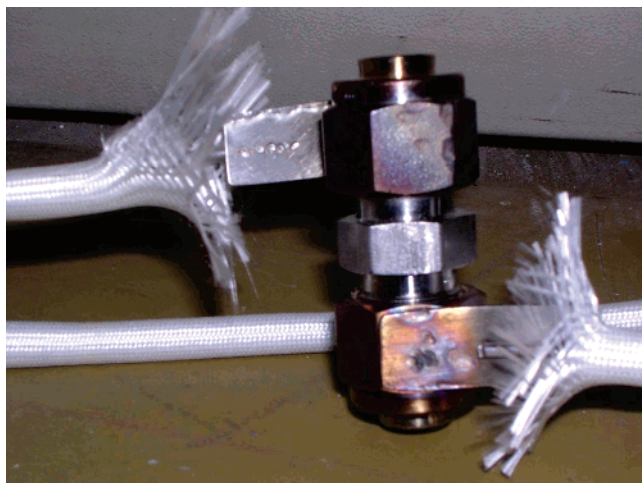


Figure 1. The Swagelok caps are attached to the conducting wires for the application of an electric field and the wires are insulated.

used for the synthesis of a variety of nanostructures.¹¹ The thermal decomposition of mesitylene at 700 °C in a closed Swagelok cell under air atmosphere produces monodispersed, $2.5 \pm 0.05 \mu\text{m}$ carbon spherules¹² (CSs). The thermal decomposition of mesitylene at 700 °C in a closed Swagelok cell under air atmosphere with an applied magnetic field¹³ of 10 T leads to the formation of long carbon filaments (CFs) up to 32 μm . In this Article, we have directed our study to the application of AC or DC electric fields during the thermal dissociation of mesitylene at 700 °C in a closed Swagelok cell under air atmosphere. The mesitylene is dissociated by dehydrogenation and separation of methyl radicals, while carbonization takes place.

The formed carbon becomes solid during the cooling process as the carbon filaments, without any support or catalyst when AC or DC electric fields were applied, and byproducts such as methane/hydrogen/carbon oxides^{12,13} were released when the Swagelok was opened.

Experimental Section: Application of AC or DC Electric Fields to the Swagelok Filled with Mesitylene

The synthesis of CFs was carried out by introducing mesitylene [97%, 1,3,5-trimethyl benzene ($\text{C}_6\text{H}_3(\text{CH}_3)_3$), bp = 162–164 °C, Aldrich Chem. Com.] into a 4 mL closed cell. The cell was assembled from stainless steel Swagelok parts. A $\frac{1}{2}$ in. union part was capped from both sides by standard plugs. The two conducting wires were attached to the caps of the Swagelok and insulated for the application of constant current, as shown in Figure 1. For this

synthesis, 1.5 mL of mesitylene was introduced into the cell at room temperature under air. The filled Swagelok was closed tightly with the other plug. The voltage was applied in such a manner that constant currents of 1.5, 3, and 5 A flowed through the Swagelok in separate experiments. An increase in the temperature of the reaction cell (Swagelok) was observed when the respective current was applied to the reaction cell. When the room temperature was 27 °C and the applied direct current was 1.5, 3, and 5 A, the temperature of the Swagelok raised to 35, 39, and 44 °C, respectively. For AC currents, the temperature varied by ± 2 °C during the application of 1.5, 3, and 5 A. The mesitylene-loaded Swageloks under the applied electric field were heated to 700 °C for 3 h. The temperature of the furnace was raised at a heating rate of 5 °C per minute. The reaction cells (Swageloks) were gradually cooled (~ 5 h) to attain room temperature. At the end of the reaction, because the electric current was still flowing through the Swagelok, the final temperature was almost the same as that at the beginning of the reactions. After the electric supply was disconnected, the reaction cells were cooled to room temperature. The cooled cells were opened, and ~ 1.17 g of a dark black powder was collected for all of the reactions. The yield of the product was 84% according to carbon wt %, and 77% according to mesitylene (C_9H_{12}). The weight loss is attributed to the formation of byproducts such as methane, water, and carbon oxides.^{12,13}

The X-ray diffraction patterns of the products were measured with a Bruker AXS D* Advance Powder X-ray diffractometer (using $\text{Cu K}\alpha = 1.5418$ radiation). An Eager 200 C, H, N, S analyzer was used for the elemental analysis of the CFs. The quantitative elemental composition of the CFs was analyzed by energy-dispersive X-ray analysis (Kevex). To ascertain whether the CFs are hollow or solid, a dry powder was immersed in an epoxy plastic (according to Spurr's formulation) and placed in a capsule to harden. The hard blocks were cut using an LKB ultratome III, and the ultrathin sections were placed on bare 400 mesh copper grids for TEM measurement of the filaments' cross-section. The morphology of CFs was determined by transmission electron microscopy (TEM) (JEM-1200EX) and high-resolution transmission electron microscopy (HRTEM) (JEOL 2010), working at acceleration voltages of 80 and 200 kV, respectively. An Olympus BX41 (Jobin Yvon Horiba) Raman spectrometer was employed, using the 514.5 nm line of an Ar laser as the excitation source to analyze the nature of the carbon in the formed product. Scanning electron microscope images were obtained using a JEOL 6300F instrument. An EPR spectrum was recorded on a Bruker EPR spectrometer (ER083 CS) operating at X-band ($\nu = 9.77$ GHz), with a 100 kHz magnetic field modulation. The electrochemical measurements were carried out using a battery test unit model 1470 coupled with a FRA model 1255 from Solartron, Inc. (driven by the Corware and ZPlot software from Scribner Associates). The alternating voltage amplitude in impedance measurements was 3 mV, and the ac frequency range used was 50 kHz to 100 Hz. All of the measurements were performed in a thermostat at 30 or 60 °C. The carbon filament (5 A DC) sample pellet was prepared at 4000 psi pressure. The surface area was measured by N_2 adsorption and calculated using a BET equation in a Micrometrics Gemini instrument.

Morphological and Structural Studies

Table 1 demonstrates the applied electric field, reaction parameters (precursor/temp/atmosphere inside cell), and the obtained morphologies of the samples observed by SEM analysis. The C, H, N, S analysis shows the presence of carbon (>99%) and a very small presence of hydrogen (<0.7%) in the CSs and the CFs. Elemental composition analysis of the CSs and CFs by energy-dispersive X-ray did

- (11) (a) Pol, S. V.; Pol, V. G.; Kessler, V. G.; Seisenbaeva, G. A.; Sung, M.-G.; Asai, S.; Gedanken, A. *J. Phys. Chem. B* **2004**, *108*, 6322. (b) Pol, V. G.; Pol, S. V.; Gedanken, A.; Goffer, Y. *J. Mater. Chem.* **2004**, *14*, 966. (c) Pol, S. V.; Pol, V. G.; Seisenbaeva, G.; Kessler, V. G.; Gedanken, A. *Chem. Mater.* **2004**, *16*, 1793. (d) Rana, R. K.; Pol, V. G.; Felner, I.; Meridor, E.; Frydman, A.; Gedanken, A. *Adv. Mater.* **2004**, *16*, 972. (e) Pol, S. V.; Pol, V. G.; Gedanken, A. *Chem.-Eur. J.* **2004**, *10*, 4467–4473. (f) Pol, V. G.; Pol, S. V.; Gedanken, A. *Chem. Mater.* **2005**, *17*, 1797–1802. (g) Pol, S. V.; Pol, V. G.; Frydman, A.; Churilov, G. N.; Gedanken, A. *J. Phys. Chem. B* **2005**, *109*, 9495–9498. (h) Pol, V. G.; Pol, S. V.; Gedanken, A. *J. Phys. Chem. B* **2005**, *109*, 6121–6125.
- (12) (a) Pol, V. G.; Motiei, M.; Calderon-Moreno, J.; Yoshimura, M.; Gedanken, A. *Carbon* **2004**, *42*, 111–116. (b) Pol, V. G.; Motiei, M.; Gedanken, A.; Calderon-Moreno, J. M.; Mastai, Y. *Chem. Mater.* **2003**, *15*, 1378.
- (13) Pol, V. G.; Pol, S. V.; Gedanken, A.; Sung, M.-G.; Shigeo, A. *Carbon* **2004**, *42/12–13*, 2738–2741.

Table 1. The Applied Electric Field with Strength, Reaction Parameters (Precursor/Temp/Time/Atmosphere Inside Cell), and the Obtained Morphologies of the Samples Observed by SEM Analysis^a

sample no.	applied field	reaction parameters precursor/temp/time/ atmosphere inside cell	sample morphology by SEM
1	no applied field	mesitylene/700 °C/3 h/air	CSs
2	1.5 A DC	mesitylene/700 °C/3 h/air	CSs + CFs
3	3 A DC	mesitylene/700 °C/3 h/air	CSs + CFs
4	5 A DC	mesitylene/700 °C/3 h/air	CFs
5	1.5 A AC	mesitylene/700 °C/3 h/air	CSs + CFs
6	3 A AC	mesitylene/700 °C/3 h/air	CFs
7	5 A AC	mesitylene/700 °C/3 h/air	CFs

^a AC: Alternating current. DC: Direct current.

not detect any other element. In all of the as-prepared samples of CSs and CFs, only carbon is observed, and no evidence is found for any other impurity. A similar pyrolytic, nongraphitic X-ray diffraction pattern¹² is observed for all of the samples (samples 1–7, Table 1).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques are used to analyze the morphology of CSs and CFs. The SEM image (Figure 2a) shows the perfect spherical and smooth surface morphology of the CSs, which possesses an average diameter of $2.5 \pm 0.05 \mu\text{m}$. Similar pictures are obtained in TEM measurements, but are not presented here. The SEM image of the

as-prepared CFs under an applied direct current of 1.5 A is shown in Figure 2b. Around 85% of the carbon is converted to CFs, and only 15% carbon remains in CS form, with an average diameter of $2.5 \mu\text{m}$. The diameter of the filaments is in the range of $2\text{--}3 \mu\text{m}$, with lengths varying from 4 to $6 \mu\text{m}$. Figure 2c shows that more than 90% of the carbon bodies are converted into filaments under an applied 3 A DC and $\sim 10\%$ is $2.5 \mu\text{m}$ -sized carbon spherules. An increase in the length of the carbon filaments up to $17 \mu\text{m}$ is observed. The SEM image of the as-prepared CFs under an applied 5 A DC field [Figure 2d] shows a filament diameter in the range of $2\text{--}4 \mu\text{m}$, with lengths varying in the range of $6\text{--}28 \mu\text{m}$. In addition to filaments, $\sim 6\text{--}8\%$ CSs [average diameter $2.5 \mu\text{m}$] is still observed. It is difficult to determine whether the CFs grow along the field direction, because after opening the Swagelok the product becomes mixed up. The histograms present the length distribution of the carbon filaments, resulting from the experiments employing 1.5 A (Figure 2e), 3 A (Figure 2f), and 5 A (Figure 2g) DC currents.

The drastic, noticeable effect of the AC current during the thermal dissociation of mesitylene at 700 °C is also detected. The carbon moieties prepared under 1.5, 3, and 5 A alternating current are shown in Figure 3a, b, and c, respectively. The SEM image of the as-prepared CFs under

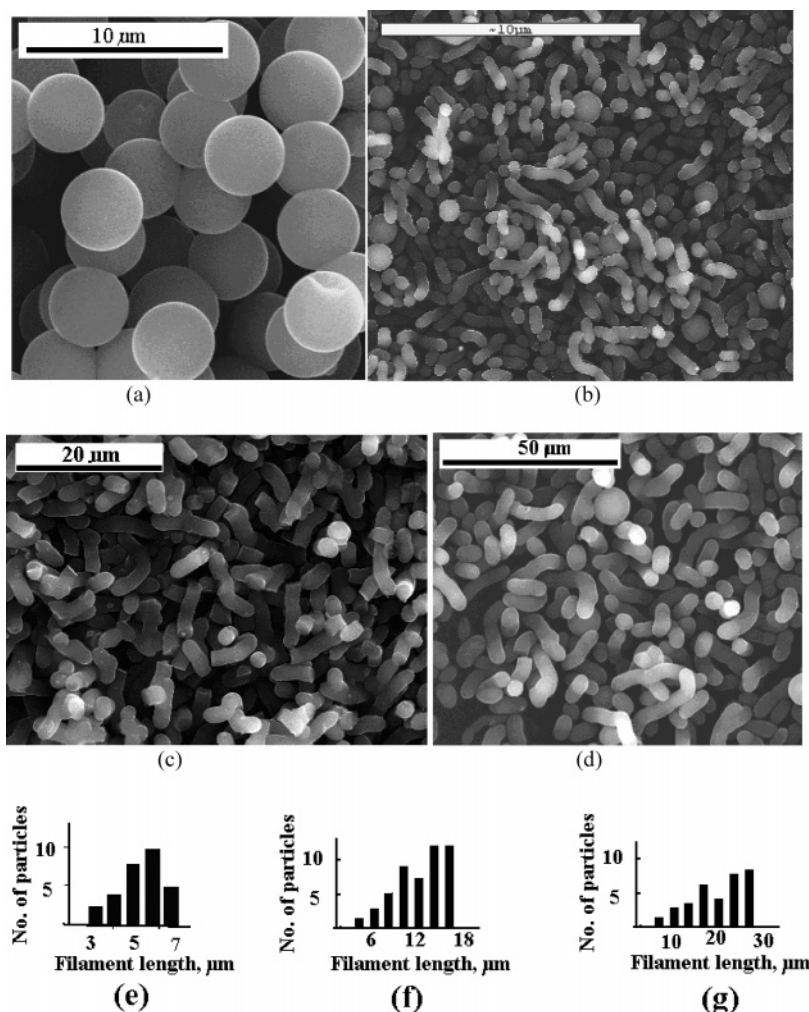


Figure 2. SEM images of (a) monodispersed CSs fabricated without applied fields, (b) CSs + CFs prepared at 1.5 A DC, (c) CFs prepared at 3 A DC, and (d) CFs prepared at 5 A DC. The histograms represent the size distribution of the carbon filaments obtained for the (e) 1.5 A, (f) 3 A, and (g) 5 A DC currents.

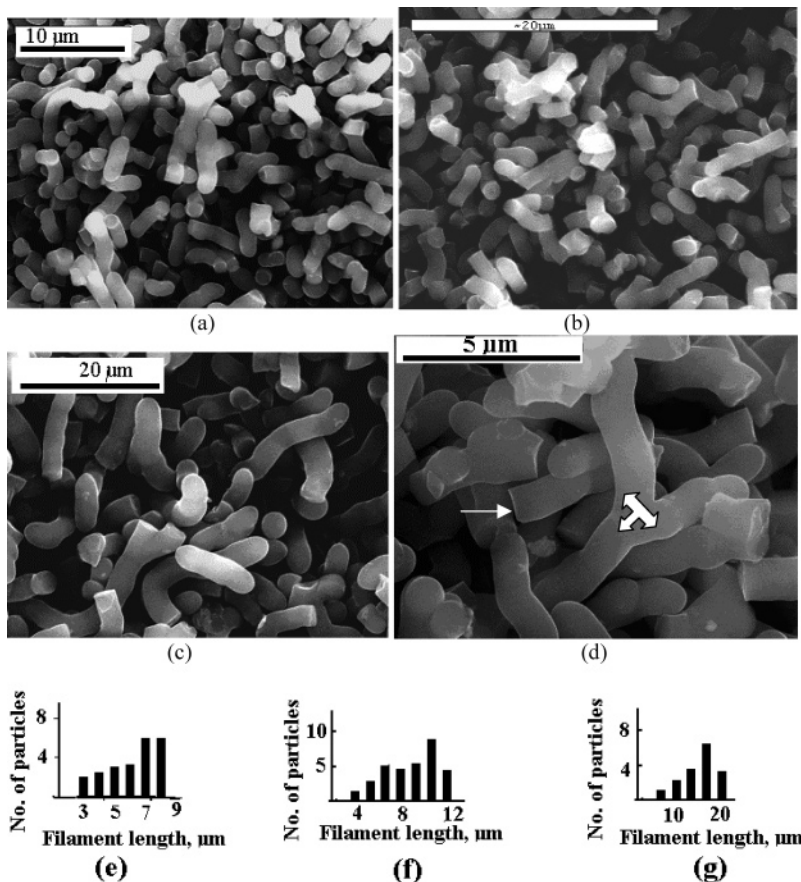


Figure 3. SEM images of (a) CSs + CFs prepared at 1.5 A AC, (b) CFs prepared at 3 A AC, (c) CFs prepared at 5 A AC, and (d) HR-SEM of CFs prepared at 5 A AC. The histogram of the carbon filaments prepared at (e) 1.5 A, (f) 3 A, and (g) 5 A AC currents.

an applied alternating current of 1.5 A is shown in Figure 3a. The carbon filaments have a diameter of ~ 300 nm and a length up to $8 \mu\text{m}$. The increase in the length of carbon filaments up to $10 \mu\text{m}$ with an increase of the AC (3 A) is also seen. The applied 5 A alternating current fabricated carbon filaments up to $20 \mu\text{m}$ in length (Figure 3c). There are numerous differences between the carbon moieties prepared in the DC and the AC fields. The distinctions between the carbon moieties prepared under alternating current are as follows: (1) Most of the carbon $\sim 98\%$ converted into filaments. (2) The ends of the filaments have a sharp edge [Figure 3d, arrow]. (3) In addition to the straight filaments, zigzag-, dipod-, and tripod [Figure 3d, triple-sided arrow]-like carbon microstructures are also formed. The HR-SEM [Figure 3d] of CFs prepared at 5 A AC demonstrates all of the three distinctions mentioned above. The histograms of the length distribution of the carbon filaments prepared at 1.5, 3, and 5 A AC currents are presented in Figure 3e, f, and g, respectively.

The TEM pictures of sample 7 prepared at 5 A AC are shown in Figure 4a–d. The zigzag [Figure 4a] type of carbon filaments has a diameter of $\sim 2 \mu\text{m}$ and a length up to several micrometers. The formation of dipod- [Figure 4b], tripod- [Figure 4c], and spanner-like [Figure 4d] carbon microstructures is observed during the application of alternating current.

To check the stress/strain, we applied 2000-PSI pressure on these samples for 20 min using a hand press, as explained below. TEM and SEM pictures revealed that under this pressure no changes in the size or shape of the carbon

moieties are observed. These results confirm that the as-prepared CSs and CFs are solid and not hollow. Figure 5 shows the semispherical tip of a carbon filament; the arrow indicates the cut edge.

HR-TEM and microtome processes are employed to understand the structural nature of the carbon filaments prepared by a 5 A DC current. Representative images are illustrated in Figures 6 and 7, clearly demonstrating that the CFs are solid (not hollow) structures, and some random arrangement of the structural units (SUs) form the filaments. Figure 6 presents circular and longitudinal cross-sections of different filaments. It can be clearly noted that longitudinal sections appear broken into pieces because their SUs are loosely joint. On the other hand, circular sections show a stronger cohesion of their SUs and keep their integrity in the microtoming process. Some cracks are observed in the circular section, running in parallel, separating different layers, of about 300 nm thickness. The higher magnification micrograph in Figure 6 shows these parallel layers, made of carbon graphitic flakes with some random arrangement.

The graphitic nature of the flakes that make up the carbon layer is clearly illustrated by electron diffraction measured on single fibers. Figure 7b shows an ED pattern of the area presented in Figure 7a. The ED pattern is typical for graphitic carbon with the two characteristic rings corresponding to the 002 and 110 planes of a graphitic lattice. We can conclude that the carbon layers observed in Figures 6 and 7 consist of randomly oriented sp^2 -bonded carbon.

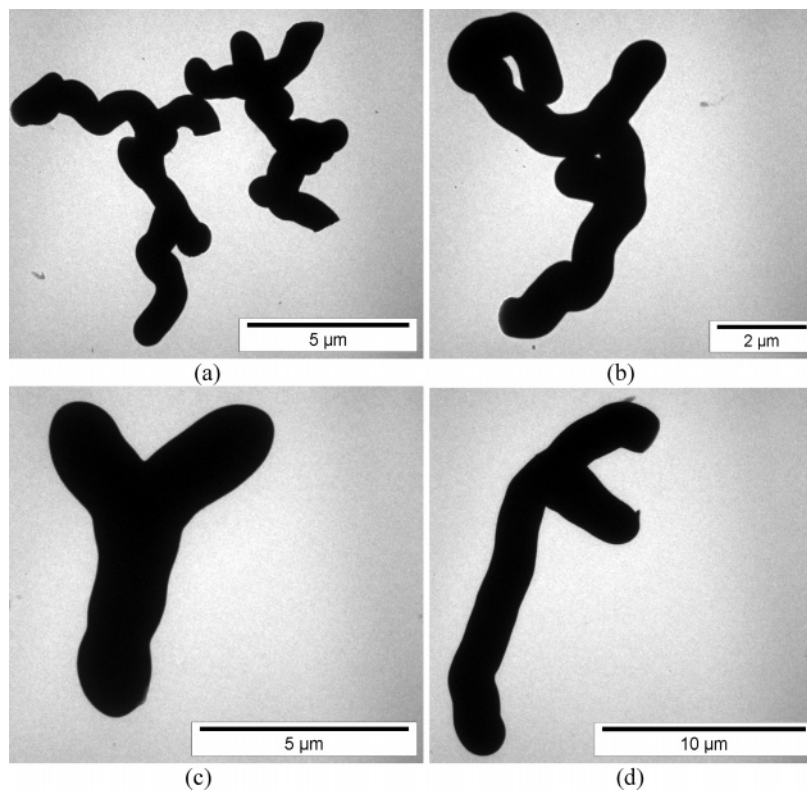


Figure 4. TEM images of a variety of carbon moieties prepared at 5 A AC electric field: (a) zigzag, (b) bipod, (c) tripod, and (d) spanner-like microstructures.

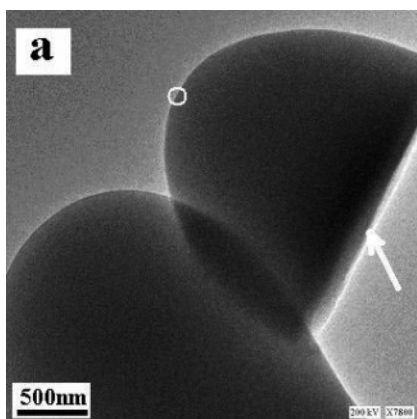


Figure 5. TEM micrograph showing the semispherical tip of a carbon filament (5 A DC).

The micro-Raman spectra of the CSs and CFs are shown in Figure 8. The D and G bands of sp^2 -bonded carbon are clearly observed for carbon spherules prepared without an electric field (Figure 8a), carbon filaments prepared at 5 A DC (Figure 8b), and carbon filaments prepared at 5 A AC (Figure 8c), respectively. The intensity ratios $I_D/I_G = 0.85$, 0.99, and 0.95 are respectively calculated for the carbon spherules prepared without an electric field, carbon filaments (5 A DC), and carbon filaments (5 A AC). These ratios indicate an amorphous carbon structure, with high content of lattice edges or plane defects within the analyzed carbon spheres/filaments.¹⁵ These similar spectra are characteristic of disordered graphitic carbon with nanosized graphitic

crystals. The D band is associated with graphitic edge-planes and carbon dangling bonds. The relative intensities of the D and G bands are generally used to estimate the size of graphitic clusters in the hexagonal plane, L_a . Our observations indicate that the graphitic clusters, which are the basic structural units in the filaments, do not grow along the a crystalline direction at higher applied electric field and that the concentration of graphitic edge-planes does not change significantly at different applied fields. The additional Raman measurements were carried out for the annealed carbon filaments (5 A DC) at 750 and 850 °C in an inert atmosphere. No drastic change in the intensity of D and G bands was observed after the annealing treatment. The graphitic layers are disordered because the growth temperature (700 °C) is not high enough to improve their local order. There is no significant change in the carbon structures prepared in DC and AC fields.

Figure 9a shows the X-ray diffraction pattern of carbon filaments prepared at 5 A DC. The interlayer spacing calculated from the 00 l diffraction lines is roughly 0.342 nm. The carbon filaments prepared at 5 A DC were further annealed at 750 °C (Figure 9b) and 850 °C (Figure 9c) in an inert atmosphere. A decrease in the main diffraction peak intensities for the 002 and 110 planes of the graphitic lattice is observed.

Electron paramagnetic resonance (EPR) spectra of the CSs and CFs samples taken at room temperature are almost the same, showing a peak-to-peak separation (ΔH_{pp}) of 40 G and a g -value¹⁴ of 2.00277. The interaction between the stable radicals that causes the growth of the carbon body to form carbon filaments is discussed elsewhere.¹³

In Figure 10, we represent impedance spectra obtained from the pelletized electrode comprising carbon filaments

(14) Mrozowski, S. *Carbon* **1988**, 26, 521.

(15) Dresselhaus, M. S.; Dresselhaus, G.; Pimenta, M. A. In *Analytical Application of Raman Spectroscopy*; Eklund, P. C., Pelletier, M. J., Eds.; Blackwell Science: Oxford, 1999; Chapter 9.

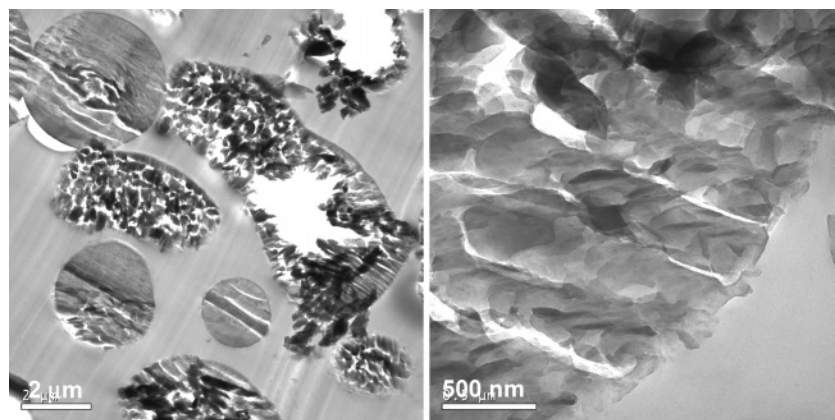


Figure 6. TEM micrographs of microtomed sample showing circular and longitudinal cross-sections of different filaments (5 A DC) and higher resolution micrograph of a circular cross-section.

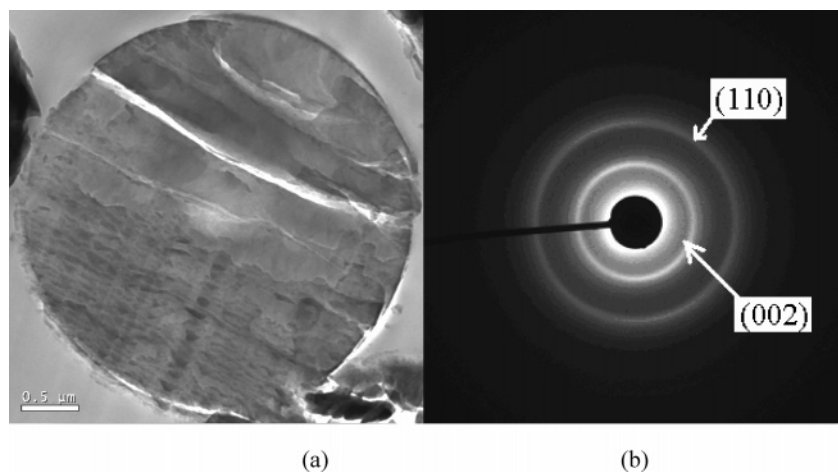


Figure 7. Electron-diffraction pattern and TEM micrograph showing the selected area for the micro-diffraction analysis, the cross-section of a carbon filament. The ED pattern shows the characteristic 002 and 110 rings of a graphitic lattice.

(5A DC). The measurements were performed initially at 30 °C, and then at 60 °C. A third impedance measurement was taken for the sample heated at 60 °C after cooling this sample back to 30 °C. First, at 30 °C, the impedance show slope lines in Z' , Z'' -coordinates, and the real part of the impedance Z' (real) decreases slightly with time at several frequencies, as indicated in Figure 11a.

As expected, the impedance at the higher temperature (60 °C) decreases in comparison with that at 30 °C. Long-term aging of the pellet at 60 °C results in minor changes of the impedance (both Z' -real and Z'' -imaginary parts), indicating that the impedance (resistance) of the pellet was stabilized due to intrinsic processes¹⁹ related to the structural and surface chemistry of carbon. This was confirmed by measuring the impedance again at 30 °C after regulating temperature from 60 to 30 °C. From Figures 10c and 11c, it is clearly seen that the impedance measured (conductivity) at 30 °C at several frequencies was stabilized (after regulating temperature from 60 to 30 °C), which may be attributed to quasi-equilibrium conditions related to the intrinsic processes¹⁹ in the pelletized electrode.

The N_2 adsorption–desorption isotherm of carbon filaments prepared in 5 A DC is presented in Figure 12. The calculated BET surface area is 2.8 m²/g, and a pore volume of 0.00022 cm³/g is recorded. We have also employed the BET surface area analysis technique to determine nitrogen gas adsorption on the surface of carbon filaments. The maximum (2.63 cm³/g) nitrogen gas adsorption was recorded at 0.9968 relative pressure (757.54 mmHg) at liquid nitrogen temperature (77 K). Therefore, at room temperature (298 K), the amount of adsorbed nitrogen on the carbon filaments is 10.2 cm³/g.

Possible Mechanistic Elucidation for the Growth of Carbon Filaments under the Application of an Electric Field

In our previous report, we demonstrated that a temperature above 600 °C is a critical temperature¹² to break C–C and C–H bonds in mesitylene using the RAPET technique. When the dissociated mixture is cooled slowly, nanographitic BSUs assemble, forming a sphere. On the other hand, when the mixture is rapidly cooled, the BSUs form a continuous “sausage-like” structure.¹²

The effect of direct/alternating currents on the formation of carbon filaments might be different. The carbonaceous substances under an applied direct current of 5 A lead to the fabrication of carbon filaments with a 2–4 μm diameter

(16) Senthil Kumar, M.; Kim, T. H.; Lee, S. H.; Song, S. M.; Yang, J. W.; Nahm, K. S.; Suh, E.-K. *Chem. Phys. Lett.* **2004**, *383*, 235–239.

(17) Banhart, F. *Nano Lett.* **2001**, *6*, 329–332.

(18) Paz, O. *Alternating Current*; Arcade Publishing: Spain, 2005.

(19) Sanchez-Gonzalez, J.; Macias-Garcia, A.; Alexandre-Franco, M. F.; Gomez-Serrano, V. *Carbon* **2005**, *43*, 741–747.

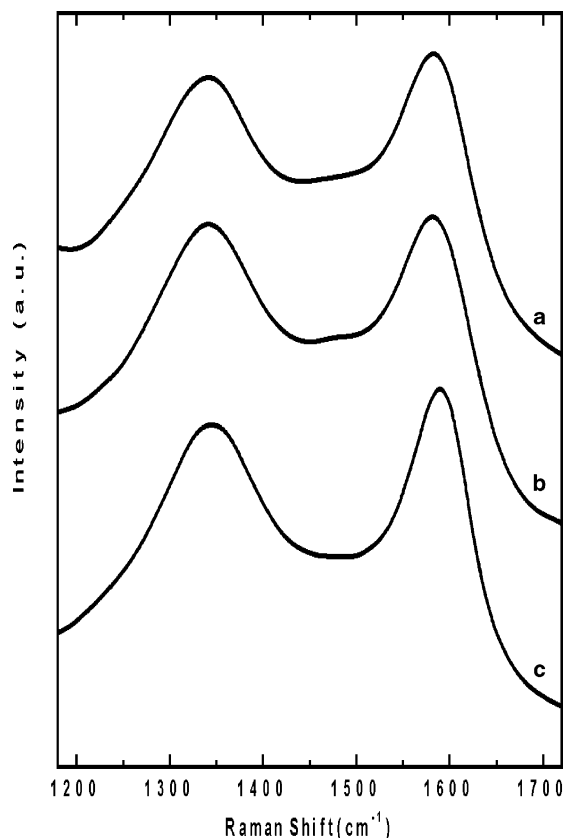


Figure 8. Raman spectra of (a) carbon spherules prepared without electric field, (b) carbon filaments prepared with electric field of 5 A DC, and (c) carbon filaments prepared with electric field of 5 A AC.

and a length up to 28 μm . Zigzag-, dipod-, tripod-, and spanner-like carbon microstructures are formed during the application of alternating current. It is known from the literature¹⁶ that the alignment of carbon nanotubes between electrodes occurs due to forces that direct the nanowires/tubes toward regions of a high electric field. The applied electric field induces electric dipoles into the nanotubes and metal nanoparticles into the suspension. In other words, the nanotubes and particles are electronically polarized¹⁶ as a result of the applied electric field. In the present fluid/fluid interface system, one fluid represents the carbonaceous mesophase, and the other represents the noncondensed phases of the dissociated products at the autogenerated pressure inside the closed stainless steel cell. The strong electrostatic forces are created on the dissociated carbonaceous products

[BSUs, aliphatic chains] during the application of the electric field. Upon cooling the sample, the interaction/collision facilitates the aggregation of BSUs to grow carbon filaments. Because of the structural anisotropy of BSUs, the induced dipole moment in the direction parallel to the length of the longitudinal axis is much stronger than in perpendicular direction, while nongraphitic carbon clusters have a uniform dipole moment irrespective of axes. Generally, the carbon nanotubes align in the direction¹⁶ of the applied electric field by adjusting themselves along tube axis (strongly polarized axis), parallel to the electric field direction. The aggregation of hydrocarbons¹⁷ and the successive transformation into amorphous carbon under the electron beam is used to solder carbon nanotubes and to make a mechanical junction.

We have also considered the possible effect of the magnetic field created by the strong electric current. An element of electric current $I d\mathbf{l}$ has an associated magnetic field, given by the law of Biot–Savart,

$$d\mathbf{B} = (\mu_0/4\pi)I d\mathbf{l} \times \mathbf{r}/r^2 \quad (1)$$

where \mathbf{r} is the unitary vector in the direction from the current element $I d\mathbf{l}$ to the point where the magnetic field is applied, r is the distance, and μ_0 is a constant ($\mu_0 = 4\pi \times 10^{-7} \text{ T mA}^{-1}$). The magnetic field is maximum next to the current and proportional to the intensity. Mesitylene is not an electrical conductor, and the current flows through the stainless steel Swagelok cell. Inside the Swagelok, the magnetic field induced will be zero at the center, simply integrating the above expression (equation 1), and will reach a maximum close to the walls. An infinite linear current of 5 A creates an integrated field ($B = \mu_0 I/2\pi r$) of a few Gauss at a few millimeters; and about a hundred Gauss ($\sim 0.01 \text{ T}$) at $\sim 100 \mu\text{m}$. The current intensity here is distributed in the circular cross-section of the cylindrical cell, and therefore the local intensity at any point in the walls of the cell is much lower than the total intensity of a linear current of the same intensity. The maximum induced magnetic field during the formation of CF inside the Swagelok is, using a gross overestimation, about a hundred Gauss. From other studies of the effect of magnetic field on the RAPET reaction of mesitylene, we know that below a magnetic field of 3 T no structural changes are observed. Thus, we conclude that obtaining CF under an electric current cannot be attributed to the magnetic field exerted inside the Swagelok.

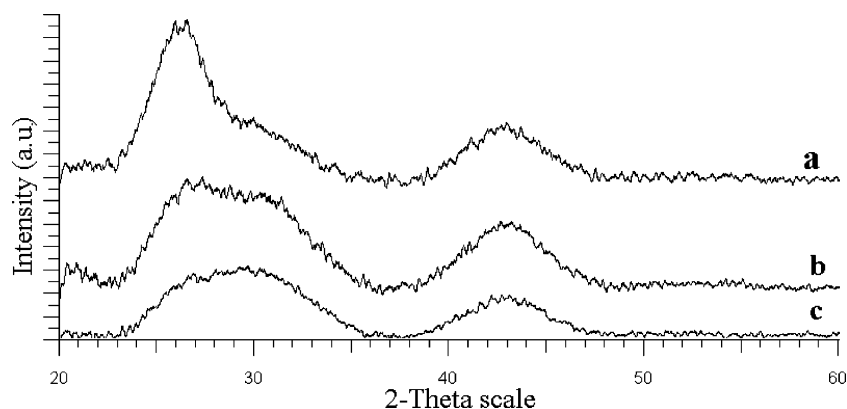


Figure 9. XRD patterns of (a) carbon filaments prepared at 5 A DC, (b) carbon filaments prepared at 5 A DC and annealed at 750 $^{\circ}\text{C}$, and (c) carbon filaments prepared at 5 A DC and annealed at 850 $^{\circ}\text{C}$ in an inert atmosphere.

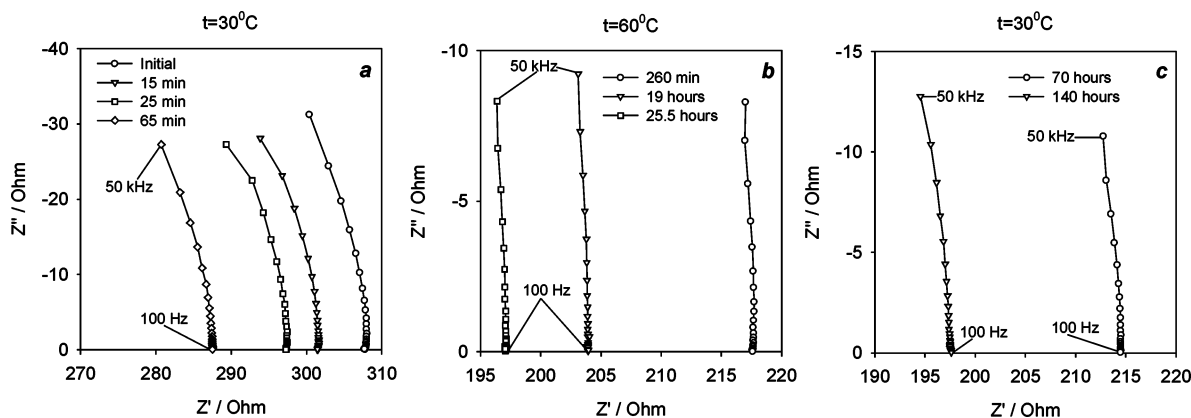


Figure 10. Impedance spectra (Nyquist plots) of the pelletized electrode prepared from the carbon filament prepared in 5 A DC. The measurement temperatures and time are indicated. Initially, the pellet (electrode) impedance was recorded at 30 °C (a), then at 60 °C (b), and, finally, at 30 °C again (c).

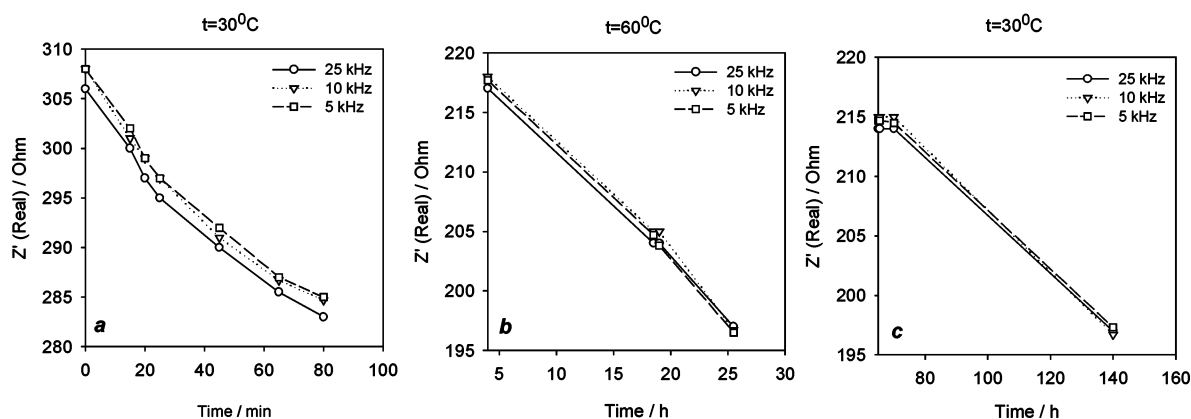


Figure 11. Evolution with time of the real part of impedance of the pelletized electrode prepared from the carbon filaments prepared in 5 A DC (see the Experimental Section).

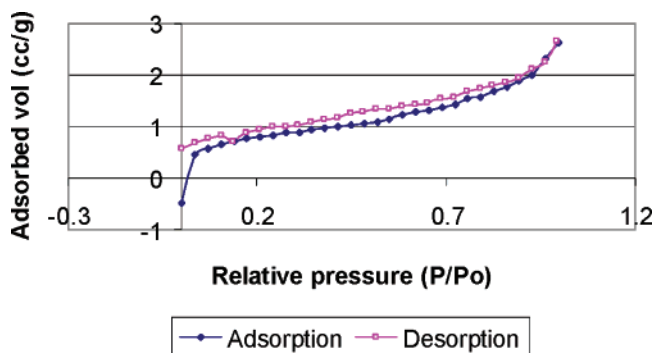


Figure 12. N₂ adsorption-desorption isotherms of carbon filaments prepared in 5 A DC.

An AC source produces currents that flow in one direction¹⁸ and then in the other, continuously cycling through peak values in either direction, that is, first positive, then negative, and so on. The AC source does not change the direction of the preferred orientation, but it does continuously change the backward and forward polarity. The polarized structural units making up the filaments find themselves continuously submitted to a mechanical torque caused by the changed polarity of the electric field in the opposite direction, in what can be described as a continuous “stirring” effect. The yield of the initial carbon content filaments increases from 85% to 98%. The continuous backward and forward stirring of the dipoles caused by the AC current

enhances the reactivity of the BSUs by increasing the mobility and number of collisions, leading to a higher yield of filaments, including the formation of zigzag and branched filaments (tripods, spanner-like).

Conclusions

The electric-field-directed growth of carbon filaments by reacting mesitylene under autogenic pressure at 700 °C without a catalyst or support is demonstrated. The thermal dissociation of mesitylene at 700 °C in a closed Swagelok cell under air atmosphere at a zero-applied electric field yields $2.5 \times 0.05 \mu\text{m}$ spherical carbon bodies that exhibit no preferred orientation. In contrast, a one-dimensional growth of carbon filaments is produced with the application of constant direct currents [DC] in the range of 1.5–5 A. In addition to the straight filaments, carbon filaments with sharp edge, zigzag-, dipod-, and tripod-like carbon microstructures and other morphologies could be fabricated with the application of AC current [1.5–5 A]. The plausible mechanism is proposed for the growth of carbon filaments under the implementation of AC or DC electric field.

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