

Magnetic field guided formation of long carbon filaments (sausages)

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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 nanodevices [1], energy storage [2], separation technologies [3] and lubricants. By very different processes, carbon nanotubes, spheres, beads, onions, glassy carbon, and pyrolytic carbon have been synthesized. All carbon materials formed from different precursors when heated to about 1300–1500 °C under reduced pressures form hexagonal layers of carbon atoms [4]. Each carbon material has a different way of aggregating upon cooling of these hexagonal layers, which leads to the formation of various textures. Recently, magnetic field-induced growth and self-assembly of cobalt nanocrystallites was studied by Niu et al. [5]. Other reports in which a chemical reaction was conducted in a magnetic field include the order observed in assemblies of superparamagnetic carrier particles reported by Rotariu [6], strain detected in iron-based ferromagnetic shape memory alloys reported by Sakamoto et al. [7] and superconductivity measured in hybrid ferromagnets [8].

In our recent publication we have discussed the synthesis of carbon spherules, its properties and the mechanism of its formation [9]. To the best of our knowledge there are no direct reports of the effect of applying a magnetic field on the synthesis of pure carbon bodies. This article shows how the magnetic field affects a reaction, which without the magnetic field leads to the formation of uniform, mono-dispersed, high purity carbon spherules (CSs) without using a catalyst. The reaction, which is the subject of this paper, is the dissociation of mesitylene at 700 °C. This reaction was studied with and without a magnetic field. Without a magnetic field it yields 2.5 µm spherical carbon bodies with a very narrow size distribution. When the same reaction is conducted under an applied magnetic field, it leads to the formation of long carbon filaments (CFs). It

is interesting to note that the dissociation of mesitylene always leads to a product with exactly the same dimensions. It is impossible to change the shape and diameter of the CSs under a wide range of reaction conditions. Different temperatures, various amounts of precursor, different surrounding atmospheres, and various heating times always yield CSs of 2.5 µm. Only after applying a high magnetic field of 10 T to the reaction cell did we get a different-shape product. We have obtained long CFs whose length varies between 10 and 32 µm. Very recently [10] we have demonstrated the effect of a magnetic field on a RAPET (reaction under autogenic pressure at elevated temperature) of MoO(OMe)₄; fabrication of MoO₂ nanoparticles coated with carbon or separated MoO₂ and carbon particles. The products of the reactions with and without a magnetic field were characterized by CHNS analysis, elemental analysis, SEM and ESR techniques. Table 1 we presents the various reaction parameters under which the reaction was conducted and the morphologies of the products.

The synthesis of CSs and CFs was carried out by introducing mesitylene [97%, 1,3,5-trimethyl benzene (C₆H₃)(CH₃)₃, bp = 162–164 °C, Aldrich Chem. Com.] into a 4 ml closed cell. The cell is assembled from stainless steel swagelok parts. A ½ in. union part is capped from both sides by standard plugs. For this synthesis, 1.5 ml of mesitylene is introduced into the cell at room temperature under air. The filled swagelok is closed tightly by the other plugs and then placed for heating at 700 °C for 3 h. The temperature is raised at a heating rate of 5 °C per minute. The reaction took place at an autogenic pressure of the precursor. The swagelok is gradually cooled (~5 h) to room temperature, opened, and 1.15 g dark black powder is collected. The yield of the product is 85% according to carbon wt% and 77% according to mesitylene (C₉H₁₂). The rest of the probable weight loss is due to the formation of byproducts such as methane, water, and carbon oxides.

The same procedure was carried out under a static magnetic field of 10 T, which was generated using a helium free superconducting magnet. The swagelok was set in the maximum magnetic point in the bore of the

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Table 1
Reaction conditions for the synthesis of carbon spherules and filaments

Sample no.	Precursor	Temp./time	Atmosphere inside cell	Morphology/TEM and size
1	Mesitylene	700 °C/3 h	Air	CSs
2	Mesitylene	700 °C/24 h	Air	CSs
3	Mesitylene	700 °C/3 h	Argon	CSs
4	Mesitylene	900 °C/3 h	Air	CSs
5	Mesitylene*	700 °C/3 h	Air	CSs
6	Mesitylene**	700 °C	Air	CSs
7	Mesitylene***	700 °C/3 h	Air	CSs
8	Mesitylene****	700 °C/3 h	Air	CFs

*After heating a swagelok at 700 °C/3 h, a very slow cooling rate, 1 °C/min.

**Very slow heating rate 1 °C/min.

***The swagelok is filled with mesitylene (>80%).

****Heating a swagelok at 700 °C/3 h under a magnetic field of 10 Tesla.

magnet, where the gradient of the magnetic field was the smallest. A ceramic oven containing the swagelok filled with 1.5 ml of mesitylene was placed between the magnetic poles. The oven was heated and cooled as in the reaction without magnetic field. The yield of the product is 76%. Scanning electron microscope images were obtained using JEOL 6300F. 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 elemental composition of the CSs and CFs was measured by energy-dispersive X-ray analysis. In all the as-prepared samples of CSs and CFs, only carbon is

observed, and no evidence is found for any other impurity. The C, H, N, S analysis shows the presence of carbon (>99%) and a very small presence of hydrogen (<0.7%) in CSs and CFs. The same pyrolytic, non-graphitic X-ray diffraction pattern [9] is observed for the CFs as the CSs.

The SEM images of the products obtained in the 700 °C decomposition of mesitylene with and without a magnetic field are presented in Fig. 1. The representative SEM image (Fig. 1a) shows the spherical morphology of the CSs, with an average diameter of 2.5 μm . Similar pictures were obtained in TEM measurements but they are not presented here. A perfect spherical shape and

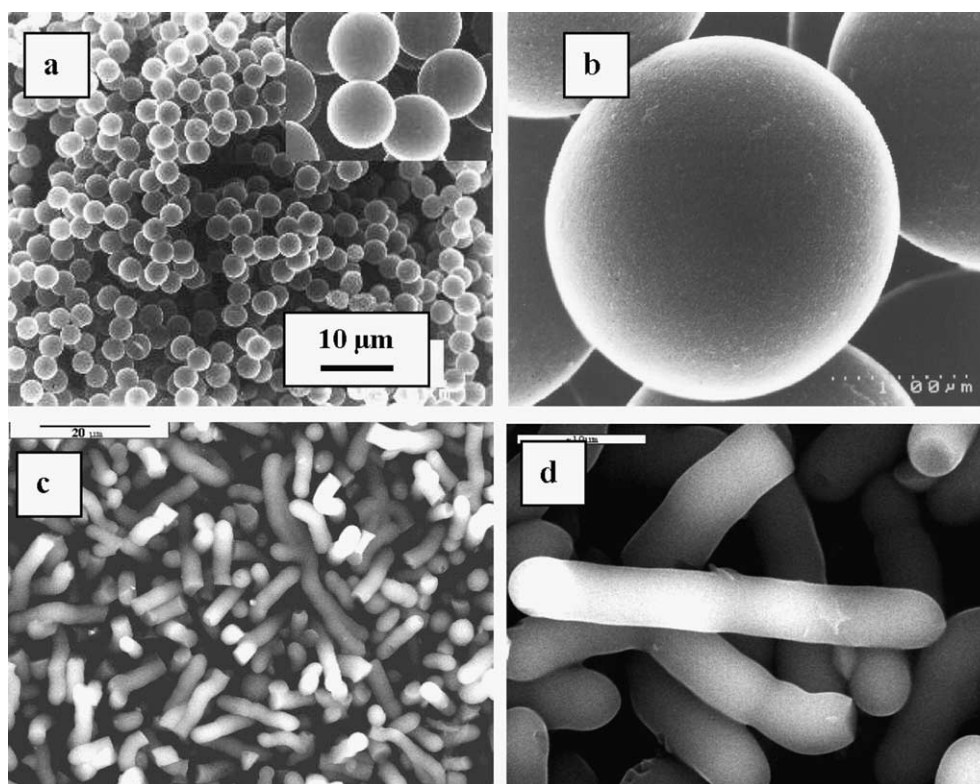


Fig. 1. SEM images of the (a) CSs and (b) CS shown at high resolution, and (c) CFs synthesized under a magnetic field and (d) CF shown at high resolution.

smooth surface can be seen at the HR-SEM picture (Fig. 1b). The as-prepared CSs are solid and not hollow, confirmed by TEM image of the horizontal cross-section of a CS. Identical carbon spherules were obtained under various reaction conditions such as different temperatures, various amounts of precursors, different surrounding atmospheres, and various heating times (Table 1).

The SEM image of the as-prepared carbon filaments under a magnetic field (Fig. 1c) shows the sausage diameter in the range of 2–4 μm , and lengths varying in the range of 10–32 μm . In addition to filaments, CSs (average diameter 2.5 μm) are also observed. Fig. 1c shows that more than 90% of the carbon bodies are converted into filaments under a magnetic field and only 10% are still 2.5 μm carbon spherules. A perfect sausage shape and smooth surface can be seen at the HR-SEM picture (Fig. 1d).

Fig. 2a shows the transmission electron micrograph of the carbon filaments synthesized under a magnetic field of 10 T. The diameter of ~ 2.5 μm and the length up to 20–25 μm is observed. The TEM of an individual CF (Fig. 2b) shown at high resolution presents a perfect sausage shape and smooth surface with the diameter of ~ 2.5 μm and length of 12 μm . The nature of the CFs is a solid and not a hollow, confirmed by TEM image of the horizontal cross-section of the CF. The sizes/shapes of the CFs observed by SEM measurements matches with the TEM measurements.

The elemental composition of the CFs and CSs are analyzed by energy-dispersive X-ray analysis. In both the as-prepared samples of CFs and CSs, only carbon is observed, and no evidence is found for any other impurity (Fig. 3).

Electron paramagnetic resonance (EPR) spectra of the CSs and CFs samples taken at room temperature are the same and are shown in Fig. 4. The g -factor is a



Fig. 3. EDAX spectrum of the CFs/CSs.

dimensionless constant and is equal to 2.002319 for an unbound electron [11]. The CSs sample showed a peak-to-peak separation (ΔH_{pp}) of 40 G and a g -value of 2.00277. This narrow paramagnetic resonance signal (width 40 G) matches well with the carbon black reported by Mrozowski [12]. He found that the width of the ESR line is inversely proportional to the concentration of the grafted radical groups. Mrozowski has published a series of comprehensive studies on the ESR of carbonaceous moieties. One of his main conclusions

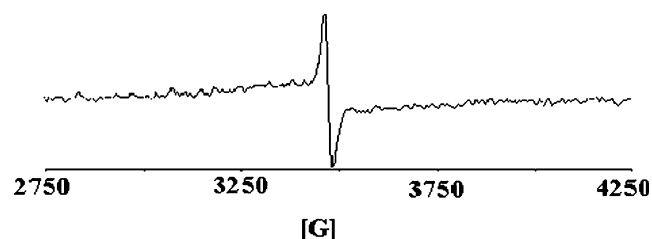


Fig. 4. Electron paramagnetic resonance exhibited at room temperature by CSs and CFs.

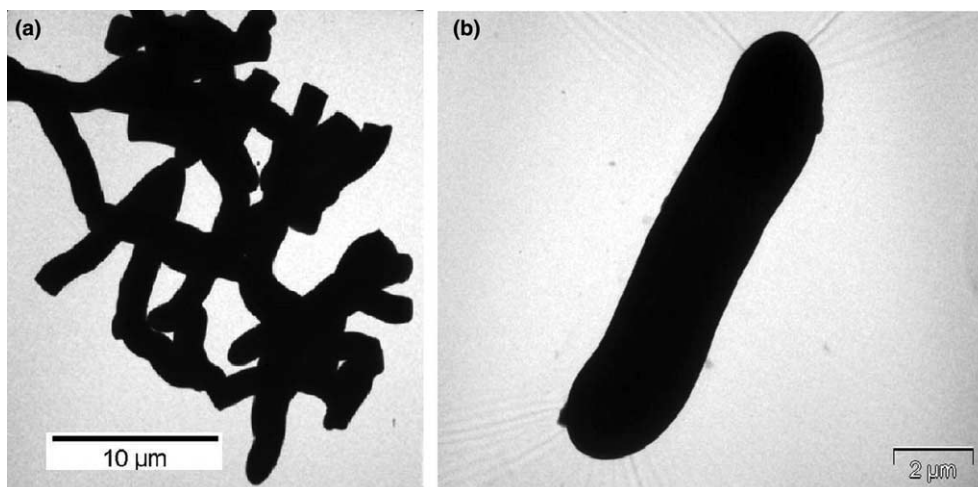


Fig. 2. TEM images of the Carbon filaments (a) synthesized under a magnetic field and (b) CF shown at high resolution.

was that all carbonaceous substances at some stage of transformation into carbons go through a phase involving formation of stable radicals [13]. The magnetic field induces the interaction between these stable radicals and causes the growth of the carbon body to dimensions of 32 μm . It also affects the longitudinal direction of the growth reflected in the formation of a long sausage. Upon the dissociation of mesitylene at 700 $^{\circ}\text{C}$, and during the three hours of heating, a spherical embryo of carbon is formed. The magnetic field directs the interaction between these small spheres, leading to the formation of the carbon filaments. It is intricate to determine whether the CFs are growing along the field direction, since after the opening of the swagelok the product is getting mixed.

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The cutting of MWNTs using gamma radiation in the presence of dilute sulfuric acid

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Carbon nanotubes (CNTs) are of great interest because of their novel structural, electronic and mechanical properties. Recently, CNTs with relatively short length in the range of 0.1–1 μm have attracted much attention because they may provide connectors and components in molecular electronic devices such as

nano-tweezers and nano-bearings. However, CNTs are usually long and tangled which limits their applications. To obtain short CNTs, many methods have been developed, such as chemical etching [1], ultrasonic treatment [2] and scanning tunneling microscope (STM) voltage [3]. These techniques have a limited yield and often create structural damage. Short single-wall carbon nanotubes with average length <50 nm could be produced by fluorination followed by pyrolysis up to 1000 $^{\circ}\text{C}$ [4], but the process is very complicated and energy

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