Electrospun Polyacrylonitrile/Poly(methyl methacrylate)-Derived Turbostratic Carbon Micro-/Nanotubes**

By Eyal Zussman,* Alexander L. Yarin, Alexander V. Bazilevsky, Ron Avrahami, and Michael Feldman

Nanotubes have great potential for applications in a rapidly increasing range of fields: catalysis, medicine, pharmacy, pheromone-release systems for crop protection, sensors, and photonics.¹⁻⁵ This is due to their high anisotropy, huge specific surface area that enhances reactivity, high rate of adsorption, and efficiency of transport processes both within and across the nanotube walls.⁶ Electrospinning is a process that produces continuous polymer fibers through the action of an external electric field imposed on a polymer solution⁷⁻¹⁰ (for a review of this process see previous publications⁹⁻¹²). To manufacture nanotubes, two fundamentally different approaches have been reported: self-assembly and template-based methods.¹¹⁻¹⁹ In the TUFT (tubes by fiber templates) process, electrospun nanofibers themselves are used as templates to produce nanotubes.¹⁴⁻¹⁹ The template-based TUFT process for nanotube production consists of three stages: i) the electrospinning of template nanofibers, ii) shell deposition via chemical or physical vapor deposition (CVD or PVD, respectively), and iii) core removal by thermal or chemical means.¹¹

Recently, a new technique was introduced that allows the co-electrospinning of polymer solutions from a spinneret containing two coaxial capillaries.²⁰ Using this technique, co-electrospinning of immiscible and miscible pairs of polymer solutions produced nanofibers with core/shell structures. This technique was then used to co-electrospin conjugated polymer nanofibers²¹ and to make the PCL/gelatin (PCL: poly(ε-caprolactone)) core/shell structure that holds great potential for controlled drug delivery and as a scaffold for tissue engineering.²² It was possible to co-electrospin almost non-spinnable polymers such as the conducting polymer polyaniline (PANi).²³ Using this same co-electrospinning technique, ceramic sol–gel precursors were added to the shell solutions to create ceramic nanotubes. The core material—a heavy mineral oil—was later extracted with octane.²⁴

The aim of the present work is to produce hollow carbon nanotubes by co-electrospinning two polymer solutions. The process was carried out in two stages. In the first stage, use was made of the non-solvent effect on one of the polymers to facilitate the creation of a solid interface between the nanofiber’s core and shell. In the second stage, the nanofibers were subjected to heat treatment to degrade the core polymer and carbonize the polymer shell.

Figure 1 shows a typical pattern of the co-electrospinning process close to the core/shell spinneret. The core-polymer capillary protrudes 0.3 to 1 mm below the shell capillary. As can be seen, the core liquid experiences a sudden increase in diameter upon exiting the capillary tube, which may be attributed to the die swell effect. Below the point of maximum swelling, the outer solution forms a thin shell that attaches to the core-polymer stream. As a result of the induced electric field, both liquids are strongly pulled into a compound Taylor cone. Numerical calculations employing the method of previous publications²⁵,²⁶ show that practically all the free charges in these ionic conductors leave the liquid/liquid interface very rapidly (compared to the residence time within the droplet) and migrate to the free surface. This result is supported by the following estimate. The characteristic charge-relaxation time is given by \[ \tau_C = \frac{\varepsilon}{4\pi \sigma_f} \] (in Gaussian, CGS units), where \( \varepsilon \) is the dimensionless relative permittivity of the solutions (\( \varepsilon = 25-30 \)) and \( \sigma_f \) is the electrical conductivity. For both

---

[*] Prof. E. Zussman, Prof. A. L. Yarin, Dr. A. V. Bazilevsky,¹¹ R. Avrahami, Dr. M. Feldman
Department of Mechanical Engineering Technion—Israel Institute of Technology Haifa, 32000 (Israel)
E-mail: meeyal@tx.technion.ac.il

[‡] Permanent address: Institute for Problems in Mechanics RAS, 101 Prospect Vernadskogo, Moscow, Russia.

[**] This work has been supported in part by the VW Fund. Supporting Information is available online from Wiley InterScience or from the authors.
solutions listed in Table 1. $\tau_c = 10^{-7}$ to $10^{-8}$ s. On the other hand, the characteristic hydrodynamic time in the droplet is given by $\tau_H = \mu a_0 / \gamma$, where $a_0$ is the characteristic droplet size and $\gamma$ is the surface tension ($10^{-2}$ m and about 21 mN m$^{-1}$, respectively). The ratio $\tau_c / \tau_H \ll 1$ guarantees that all the charges rapidly migrate to the free surface. Their presence produces electric Maxwell stresses that stretch the outer liquid (i.e., the shell). As a result, in the cases with equal flow velocities through the core and shell nozzles, the inner liquid (the core) would be entrained only by the viscous forces. However, the high viscosity of the core liquid and interfacial tension can degrade the entrainment process. The above-mentioned numerical calculations that all the charges rapidly migrate to the free surface. Therefore, buckling arose from distributed friction forces acting on the core from the shell in those instances when the core liquid left the nozzle faster than the shell liquid. The buckling can be described in a manner similar to that in previous publications such that the predicted characteristic buckling “steps” (cf. Fig. 2) are of the order

$$\frac{\Delta L_{i+1}}{a} = K \cdot \left( \left| U_{i+1} \right|^{3/4} - \left| U_i \right|^{3/4} \right)$$  \hspace{1cm} (1)

where $U_i = -4.233, -7.86, -11.49, ... \ (i=1,2,3, ...)$ are the roots of the equation

$$\exp \left( \frac{3}{2} U_i \right) = \sqrt{3} \sin \left( \sqrt{3} U_i \right) + \cos \left( \sqrt{3} U_i \right)$$  \hspace{1cm} (2)

and $a$ is the core cross-sectional radius; the dimensionless factor $K$ is dependent on the ratio $A/a$, where $A$ is the shell cross-sectional radius.

To quantify the scale of the existing core “steps” in the collected microfibers, we estimated a discrete-time signal vector and calculated the mean-square spectrum (i.e., the distribution of power over frequency) that has a property containing the mean-square (power). The detailed analysis is presented in the Supporting Information. For the core path (signal) in Figure 2, the length scale (buckling “steps”) of the main signal has a wavelength of 52.6 $\mu$m (standard deviation, STD = 13.5 μm) with a significant additional nonlinear distortion (for details see the Supporting Information).

Table 1. Characteristic properties of test materials: weight-average molecular weight ($M_w$), weight concentration ($C$), electric conductivity ($\sigma_e$), zero-shear viscosity ($\mu$). Relaxation times of spinnable polymer solutions are of the order $\theta = 0.01$ to 0.1 s [27,28].

<table>
<thead>
<tr>
<th>Location</th>
<th>Material</th>
<th>Solvent(s)</th>
<th>$C$ [%]</th>
<th>$\sigma_e$ [mS m$^{-1}$]</th>
<th>$\mu$ [cP]</th>
<th>Flow rate [mL h$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell</td>
<td>PAN</td>
<td>DMF</td>
<td>12</td>
<td>3.5</td>
<td>6700</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core</td>
<td>PMMA</td>
<td>Acetone/DMF</td>
<td>15</td>
<td>0.3</td>
<td>3800</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Optical image of collected compound microfibers with buckling of the core jet inside the shell (the fibers are resting on an aluminum substrate.) The signal decomposition shows the main signal has a wavelength of 52.6 $\mu$m (standard deviation, STD = 13.5 μm) with a significant additional nonlinear distortion (for details see the Supporting Information).
age, where large volumes and interfacial areas inside hollow fibers might be beneficial.

In most of the cases studied, the customary bending instability\[8\] set in between the droplet tip and the ground, and as-spun core/shell nanofibers similar to those shown in Figure 3a were obtained. The borders between the core and shell are easily seen, with the core diameter and shell wall thickness measuring 2.1 and 2.6 µm, respectively. On average, the core diameter was 1.9 µm (STD = 0.2 µm), and the shell diameter was 6.5 µm (STD = 0.8 µm). The images of the as-spun fibers suggest that core buckling could also be initiated inside relatively thin shells. Indeed, in some cases, the core can be seen protruding through the shell and forming an arch or bulge-like structure (see Figs. 3b,c). However, the incidence of these phenomena is fairly insignificant and can be strongly suppressed by small confinement inside a relatively thin shell.

Figure 4 shows a scanning electron microscopy (SEM) image of broken as-spun core/shell fibers that had been coated with gold to enhance image capture. The figure clearly indicates formation of a core/shell structure. The core diameter, however, is narrower than the inner diameter of the shell, which apparently is due to the relatively higher vapor pressure of acetone in the core compared to that of dimethylformamide (DMF) in the shell. The inner envelope of the shell looks uniform and was not damaged even though the core had either shrunk faster than the shell, or the shell had been inflated by the rapidly evaporating acetone. Acetone is a not a solvent for polyacrylonitrile (PAN). Therefore, a homogeneous PAN solution in contact with acetone separates into two phases: a PAN-rich phase and a phase less rich in PAN. The former solidifies and forms a rigid structure with probably some degree of porosity. Our assumption is that, during the co-electrospinning process there is an interaction between PAN and acetone (non-solvent), which stabilizes the interface between the core and shell due to precipitation of PAN. This may be crucial for the formation of a robust core/shell structure. Note that in the experiments using poly(methyl methacrylate) (PMMA)/pure DMF core solutions of various concentrations we have, to date, not succeeded in achieving a good core/shell structure.

Subsequently, the collected as-spun fibers were stabilized in air at 250 °C and then heated in stages to 1100 °C in an inert nitrogen atmosphere. The PAN in the shell carbonized, forming a turbostratic carbon structure.\[32\] The mechanical and structural characterization of electrospun PAN-derived carbon nanofibers were presented previously.\[32\] The bending modulus, \(E\), of the carbonized fibers was determined using the natural resonance vibration method and found to be 63 GPa. The fracture strength of the electrospun PAN-derived carbon nanofibers was obtained previously\[32\] through a tensile test. The average fracture strength was 0.64 GPa. Since the material and the processing parameters are identical in this work and in a previous publication,\[32\] it is assumed that the carbonized hollow fibers have similar mechanical properties. Based on previous works,\[33,34\] we can also hypothesize that the fibers will have voids elongated in the axial direction with a porosity of up to 18 %. Simultaneous to these processes, the PMMA in the core undergoes a variety of intrinsic thermal-degradation processes—depolymerization, random scission, and side-group elimination—that produce volatile degradation products.\[35\] No residues of PMMA were observed with high-
resolution SEM (HRSEM) at the end of the carbonization process. According to a previous publication,[35] PMMA has been shown to degrade cleanly (i.e., with negligible carbon residue <0.2 wt.-% when heat-treated in an inert atmosphere to 1000 °C) over a narrow temperature range and in vacuum or inert atmospheres, to yield almost 95–100 % pure monomer. Free-radical-polymerized PMMA begins to decompose at around 270 °C, starting with the double bonds at the ends of its chain. An oxidative atmosphere initially inhibits decomposition of PMMA (200–300 °C), however, at higher temperatures it accelerates decomposition by enhancing random scission events.[36] The activation energy of PMMA decomposition is about 120 to 200 kJ mol⁻¹, depending on the end group.[37] As heat is applied and the PMMA in the core begins to degrade, volatile constituents such as residual solvent and low-molecular-weight components (e.g., monomers) penetrate the core/shell interface and diffuse to the outer surface of the shell, where they evaporate. In those cases in which gas transport through the shell layer is blocked due to either relatively high shell thickness or low permeability, the internal pressure in the core increases, resulting in internal circumferential stresses in the shell. Obviously, this type of pressure build-up occurs only if the ends of hollow fibers are blocked and the shell is substantially intact. The pressure build-up can be estimated using Antoine’s equation.[38] At the absolute temperature of 550 °K (277 °C) the pressure of the methyl methacrylate (MMA) monomer vapor can reach 3.5 MPa.[39] The pressure value is of the order of water-vapor pressure inside carbon nanotubes produced by the hydrothermal method, 30 MPa.[40,41] Assuming a pressure drop Δp of about 3.4 MPa acting on a hollow fiber wall with a radius a = 0.5 µm and a thickness h = 0.03 µm, in the framework of the thin-shell approximation, we find the circumferential stress on the wall to be[42]

$$\sigma_{00} = \frac{\Delta p a}{h}$$

which yields $\sigma_{00} = 0.056$ GPa. This value is lower than the average fracture strength of turbostratic carbon, 0.64 GPa; however, still local imperfections of the hollow fiber may yield lower fracture strength, and then the hollow fiber wall is susceptible to breakage due to the encapsulated vapor high pressure. Moreover, we have used the lowest pressure estimate, whereas the pressure will rapidly increase at higher temperature. As the images discussed below show, this process does indeed occur. Figure 5 shows SEM images of several broken carbonized PAN fibers after being heated. These images clearly demonstrate the formation of hollow tubular structures. The average inner diameter is 500 nm (STD = 100 nm) and the average wall thickness is 200 nm (STD = 50 nm). The core hole is relatively concentric with the shell, with the occasional off-set probably resulting from core buckling during the initial formation of the as-spun fibers. Figure 5c shows an SEM image of a sample which was collected as a uniaxially aligned array using the technique described in a previous publication.[43] In several of these carbonized nanotubes, the core eccentricity relative to the shell resulted in protruding arches (Figs. 5c,d).

The technique described by Theron et al.[43] employs an electrostatic lens—a grounded rotating wheel with a very sharp edge, where uniaxially aligned nanofibers are accumulated. Single nanofibers, approximately tens of centimeters long, can be relatively easily detached from the wheel, as has

![Figure 5](http://www.advmat.de)
been done for tensile tests.\cite{44,45} Such a single core/shell nanofiber can be electrospun and carbonized using the technique of the present work, which should result in carbon nanofibers of several tens of centimeters long.

The intriguing question as to how decomposed PMMA escapes from the extremely long and not-highly-porous carbonized shells is resolved by examining Figures 5e,f where holes in the wall of otherwise-intact nanotubes are clearly seen. These shell-fracture patterns agree with the circumferential-stress estimate for the shells given above. Two kinds of fractures are observed. In Figure 5f the holes are almost perfect, which may be indicative of a bubbling of the PMMA during an early stage of the heating process when the shell is still ductile. Formation of such holes serves to reduce gaseous pressure and obviate the need for gases to travel long distances along the shell. Fortunately, inspection of the carbonized nanotubes shows that there are sufficiently long undamaged sections of the nanotube that can be used in potential applications.

In summary, we have developed a simple two-stage technique for producing long, strong, carbonized micro-/nanotubes via polymer–polymer co-electrospinning. In this paper, the physical mechanisms underlying the formation of carbon nanotubes via co-electrospinning are explained and the development of several applications for turbostratic carbon micro-/nanotubes is discussed. In addition, we discovered microtubes whose structures provide extremely high confinement volumes, a property which is of potential use for hydrogen storage. The development of other applications of nano- and microtubes is already underway.

**Experimental**

To produce the nanotubes, we used the co-electrospinning process described by Sun et al.\cite{20}. The set-up consisted of core and shell capillaries. The core capillary was a stainless-steel needle with inner and outer diameters of 0.42 and 0.64 mm, respectively. The shell capillary was a plastic needle with inner and outer diameters of 1.2 and 1.75 mm, respectively. The tip of the core capillary protruded 0.3 to 1 mm below that of the shell capillary. The procedure used to determine the optimal distance for setting the position of the core capillary is discussed in the main text. The polymer system used for co-electrospinning is shown in Table 1. All materials were purchased from Aldrich and used without further purification.

During co-electrospinning, the solutions were subjected to an electrosstatic field of about 0.3 kV cm\(^{-1}\), and the as-spun core/shell nanofibers were collected on an aluminum foil that was placed 18 cm below the tip of the core needle (for additional details see the work of Theron et al.\cite{43}). The steel needle was connected to a high-voltage power supply (Gamma High Voltage, XRM30P); the solutions were fed by two syringe pumps (Harvard, PHD 2000; Aites, Infutech 610/A). All experiments were conducted at room temperature in air with a relative humidity of ~42 %. The carbonization process was carried out as follows: the as-spun core/shell nanofibers were placed on alumina substrates in a tube furnace and stabilized in air for 30 min at 250 °C. The fibers were then carbonized by heating in nitrogen first at 750 °C for 1 h, and then at 1100 °C for another hour. The ramp rate was 5 °C/min\(^{-1}\) between the 250, 750, and 1100 °C plateaus. After that, the specimens were manually broken and then deposited on the carbon tape. Images were obtained by means of secondary scattered electrons using a Leo Gemini 982 high-resolution scanning electron microscope at an acceleration voltage of 2 to 4 kV and a sample-detector distance ranging from 1 to 4 mm. For some of the micrographs, as-spun fibers were coated with a thin gold film by means of a sputtering process in order to increase their conductivity. The samples were also observed using an optical microscope (Olympus BX51) with a magnification of \(\times1000\), and a digital camera (Olympus DP12 with resolution of 3.34 million pixels).

Received: June 6, 2005
Final version: September 11, 2005
Published online: January 10, 2006

\[\text{[10] A. Frenot, I. S. Chronakis, Curr. Opin. Colloid Interface Sci. 2003, 8, 64.}\]
\[\text{[11] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, Compos. Sci. Technol. 2003, 63, 2223.}\]
*Carbon* 2005, 43, 2175.


