

with a Siemens P4 four-circle diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7103 \text{ \AA}$ ).

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## Compound Core–Shell Polymer Nanofibers by Co-Electrospinning\*\*

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The preparation of organic–inorganic materials and semiconductor systems that are functionalized via a structuring process on the submicrometer scale—nanotechnology—is currently an area of intense activity both in fundamental and applied science on an international scale. For a broad range of applications, one-dimensional (1D) systems, i.e., fibers and hollow fibers (tubes), are of fundamental importance.<sup>[1]</sup> The manufacturing of structured yet compact polymer fibers with diameters from the submicrometer range down to 10 nm meets with considerable interest for various kinds of applications. Examples are nanofibers for various filter applications and protective clothing, composite-fiber-reinforced materials, biomedical applications (tissue engineering, drug-release systems), fibers loaded with catalysts, core–shell fibers for optical applications (waveguides), or nanocables for microelectronics applications. The reduction of the diameter into the nanometer range gives rise to a set of favorable properties, including the increase of the surface to volume ratio, variations in the wetting behavior, modifications of the release rate, or a strong decrease in the concentration of structural defects on the fiber surface, which will enhance the strength of the fibers.

More recently, core–shell fibers, as another type of a 1D nanostructure, have gained interest, since core–shell structures could further enhance material property profiles for the

above-mentioned applications. Examples reported up to now are core–shell fibers made of conducting materials such as metal, semiconductor, and conducting polymers in the core (e.g., Au,<sup>[2]</sup> Ag,<sup>[3]</sup> Ni,<sup>[4]</sup> Si,<sup>[5]</sup> SiC,<sup>[6]</sup> CdSe,<sup>[7]</sup> and polypyrrole<sup>[8]</sup>) wrapped by silica<sup>[2,3,5,6]</sup> or polymers.<sup>[2,4,7,8]</sup> The nanocables were fabricated by laser ablation,<sup>[9]</sup> polymerization of monomers on a template,<sup>[8]</sup> and growing a semiconductor nanowire inside the polymer tubules.<sup>[10]</sup> Nano- and mesocables made of polymer–metals and polymer–polymer (conducting polyalkylthiophenes) were also obtained by the TUFT-process (tubes by fiber templates).<sup>[11–13]</sup>

Spider silk represents a well-known example of compound core–shell fibers, possessing a combination of mechanical properties seen in no other fibers.<sup>[14,15]</sup> Co-extrusion is used to spin compound chemical fibers and core–clad polymer or glass optical fibers.<sup>[16]</sup>

Another promising route to new materials based on core–shell fibers is represented by electrospinning. Electrospinning attracts great attention as a versatile method for processing of polymer fibers with diameters in the sub-micrometer range.<sup>[17]</sup> Electrospinning proceeds when a high enough electric field is applied to a pendant or sessile droplet of a polymer solution or melt. In a typical experimental set up, a polymer solution or melt in a syringe with a metal needle and a counter electrode are kept at an electric potential difference of the order of several kilovolts. By action of the electric Maxwell stresses the polymer solution or melt forms a jet, which is stretched by the bending instability and further on solidifies into an ultra-thin fiber. Following this general concept a variety of polymer fibers were prepared for a variety of different applications including templates for nanotubes, electrical conductivity, photocatalysis, drug delivery, etc.<sup>[18]</sup>

The present work describes the processing of core–shell nano-/mesofibers by co-electrospinning of two materials. Compound capillary liquid–liquid jets of Newtonian, non-polymeric fluids were first introduced in relation to ink-jet printing.<sup>[19]</sup> In the present approach, however, both liquids outflowing from the core- and the surrounding concentric annular nozzles are polymer solutions or a combination of polymer solution and melt. A compound droplet sustained at the edge of such compound nozzles should undergo transformation into a compound Taylor cone with a compound jet co-electrospun from its tip. Then, as in the ordinary electrospinning process, the jet will be pulled by the electric field, and stretched by the bending instability far enough from the droplet. Solvent will evaporate and the compound jet will solidify, resulting in compound core–shell nanofibers. The co-electrospinning process is expected to be fast enough to prevent any mixing of the core and shell polymers, as well as of any compounds staining them. Co-electrospinning is of particular interest for those core materials that will not form fibers via electrospinning by themselves. Here, the shell polymer can serve as a template for the core material leading to cable-type structures. Core–shell fibers of this type will certainly foster applications, e.g., in the field of microelectronics, optics, and medicine, which justifies intensive research in this direction.

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Co-electrospinning can also facilitate manufacturing of polymer nanotubes, and it allows one to eliminate the vapor deposition stage characteristic of the three-stage TUFT-process,<sup>[18f,h,i]</sup> and to develop a novel two-stage process.

The experimental set-up is characterized by a polymer storage bath with two air inlets (Fig. 1), a high voltage power supply, and a grounded, flat copper collector; details are given in the experimental part. Due to pulling by the electric Maxwell stresses, the polymer solutions were released at the bottom of the bath through two concentric openings.

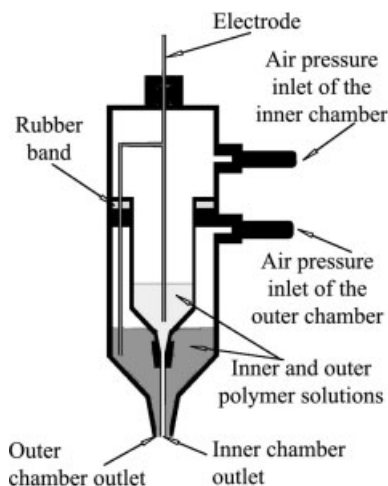


Fig. 1. Experimental set-up used for co-electrospinning of compound core-shell nanofibers.

Core-shell fibers made of two identical polymers (2 or 3 wt.-% poly(ethylene oxide), PEO) were processed in one type of experiment. In this case, different amounts of bromophenole (0.2 to 2 wt.-%) were added to the polymer solutions in water-ethanol mixtures in order to gain optical contrast. The total diameters of the compound PEO-PEO fibers contrasted by bromophenole amounted to about 3000 nm (Fig. 2). The core-shell structure can clearly be seen. Sections of the compound fibers as long as about 100  $\mu\text{m}$  are clearly seen. The core diameter in the compound fiber is about 2000 nm. Undesirable mixing of the dyeing agent can obviously be prevented by the low diffusion coefficients rela-

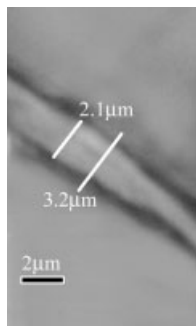


Fig. 2. Optical microscope photograph of a compound nanofiber. Core and shell polymer solutions 2 wt.-% PEO ( $M_w = 10^6$ ) in ethanol/water (4:6) mixture. The core and shell are different colors because of the presence of bromophenole at different concentrations; 2 and 0.2 wt.-%.

tive to the fast enough stretching and solidification processes taking place in the spinning process.

In a second type of spinning experiment, compound fibers were prepared from two different polymers. Compound nanofibers electrospun from 3 wt.-% PEO-8 wt.-% polysulfone (PSU) solutions had an outer diameter of the order of 60 nm, and a core diameter of about 40 nm, as apparent from Figure 3. Thicker fibers (of the order of 800 nm) were also obtained, however transmission electron microscopy (TEM) studies did not succeed in revealing their inner structure. The

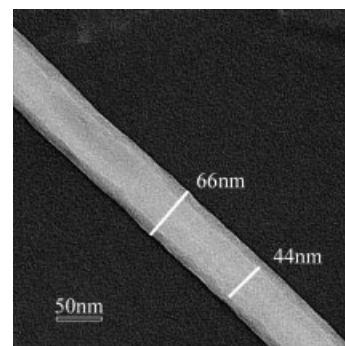


Fig. 3. TEM of a compound nanofibers. Core and shell solutions are PSU and PEO, respectively.

compound nanofiber shown in Figure 3 demonstrates a relatively smooth core-shell interface. In some cases, however, the interface was perturbed, due to an onset of instability.

In a similar way, core-shell fibers were obtained from PEO (shell) and poly(dodecylthiophene) (PDT, core) by co-electrospinning of a 2 wt.-% solution of PEO in chloroform and a 1 wt.-% solution of PDT in chloroform. TEM investigations of the PEO-PDT coaxial fibers showed strong contrasts between core and shell, since the TEM contrast of PDT is much stronger compared to PEO due to the presence of sulfur (Fig. 4). The total fiber diameter is about 1000 nm, whereas the diameter of the core region is about 200 nm. A contamination of the core region by PEO cannot be fully ruled out at

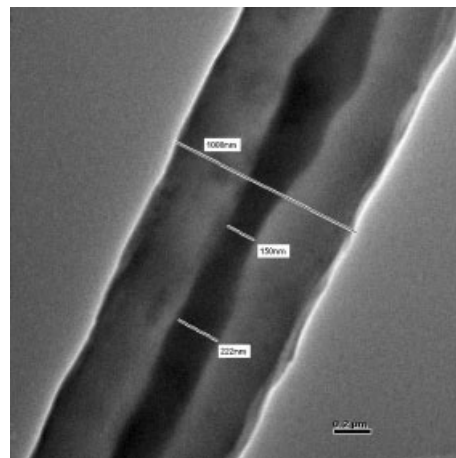


Fig. 4. TEM of unstained samples of co-electrospun PEO (shell) and PDT (core).

this stage but it is obvious from the TEM images that coaxial fibers of PEO and PDT were formed.

It is important to stress here that the PDT used in these experiments did not form fibers by itself in electrospinning due to its low molecular weight. However, fibers were now obtained by co-electrospinning. Obviously, the PEO shell served as a template for the formation of the PDT fibers.

Co-electrospinning can also be applied to polymer-metal salt systems. A 3 wt.-% poly(L-lactide) (PLA) chloroform solution was co-electrospun with a 5 wt.-% solution of  $\text{Pd}(\text{OAc})_2$  in tetrahydrofuran. In order to generate metallization, the coaxial fibers were annealed for 2 h at 170 °C, which caused conversion of  $\text{Pd}(\text{OAc})_2$  into elemental Pd.

TEM investigations of the annealed coaxial fibers clearly proved the core-shell fiber morphology (Fig. 5). The outer diameter of the coaxial fibers is about 500 nm and the diameter of the core phase is about 60 nm.  $\text{Pd}(\text{OAc})_2$  does not form

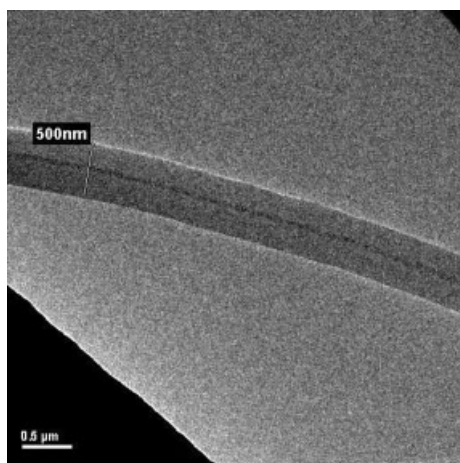


Fig. 5. TEM of annealed (170 °C/2 h) unstained samples of co-electrospun PLA and  $\text{Pd}(\text{OAc})_2$ .

fiber-like structures upon electrospinning but obviously fiber-like structures can be obtained by co-electrospinning with PLA. PLA thus induced a 1D arrangement of Pd.

It is obvious that co-electrospinning can be successfully used for the formation of coaxial fibers made of pairs of different materials PEO-PDT, PLA-Pd, and PEO-PSU, or of pairs of identical polymers (PEO-PEO) contrasted by dyeing agents such as bromophenol. In the case of PEO-PDT, PLA-Pd, and PEO-PEO pairs, the total fiber diameters reported here were slightly larger than those in the typical range of electrospun fibers. Yet it has been shown in the past that the diameters can be controlled via suitable selections of concentration, molecular weights, and conductivities of the solution. On the other hand, in the case of PEO-PSU nanofibers, total diameters could be obtained that were smaller (about 50 nm) than those for the conventional electrospun nanofibers. It is of particular interest that non-electrospinnable materials like PDT and  $\text{Pd}(\text{OAc})_2$  can be forced into 1D arrangements by co-electrospinning using a good fiber forming shell polymer. The method of co-electrospinning should be

very versatile for the processing of a wide variety of systems different from those presented here and will certainly foster new materials design. It can also result in a novel two-stage method of fabrication of hollow nanofibers (nanotubes) instead of the previously used three-stage process. Co-electrospinning should be followed by a selective removal of the core material in the compound fiber via selective solvents or heat treatment.

The existing theory of the electrostatically driven bending instability leading to enormous elongation of polymer jets and formation of nanofibers in electrospinning allows for the estimate of the effect of the zero-shear viscosity and viscoelasticity, polymer concentration, solvent composition, and applied voltage on the characteristic time of fiber formation and their final cross-sectional radii.<sup>[17a,c]</sup> The theory, however, deals with only a single polymer in the fiber. Its generalization for the case of core-shell fibers, similar to that for the capillary jets, described by Hertz and Hermanrud,<sup>[19]</sup> can be foreseen in future along the same lines as described by Reneker and co-workers.<sup>[17a,c]</sup> Even without detailed calculations, it is clear that the characteristic time of the bending instability of the order of  $\tau_1 = 1$  ms should, however, be similar in the co-electrospinning case. During this time, a jet element is looped and strongly stretched, as well as partly solidified due to solvent evaporation. This time should be compared to the characteristic time of the diffusion spreading of a sharp boundary between two identical polymers doped by different dyeing agents  $\tau_2 = d^2/D_a$  (with  $d$  being the nanofiber cross-sectional diameter and  $D_a$  the diffusion coefficient of the dopant). The time  $\tau_1$  should also be compared to the characteristic time of spreading of a sharp boundary between two different polymers due to their mutual diffusion,  $\tau_3 = d^2/D_p$  (with  $D_p$  being the polymer diffusion coefficient). Taking for the estimate  $d \sim 10^{-6}$  m,  $D_a \sim 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, and  $D_p \sim 10^{-13}$  to  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup>,<sup>[20]</sup> we obtain  $\tau_2 \sim 10^{-2}$  s and  $\tau_3 \sim 10^{-2}$  to 1 s. Since both  $\tau_2$  and  $\tau_3$  are larger than  $\tau_1$ , all the sharp boundaries should survive in the co-electrospinning in agreement with the experimental results of the present work.

The entrainment of a non-spinnable component in co-electrospinning is related to the internal (viscous and viscoelastic) stresses and the electric Maxwell stresses, which could be developed in such a material. For some materials, the entrainment of the core material by a spinnable outer shell is possible, as the present experiments showed. However, in the case of air as a core fluid (which is attractive for direct co-electrospinning of hollow nanofibers) the internal viscous forces and the electric Maxwell stresses in air are too low, and the continuous process cannot be sustained, as was shown in the present work.

## Experimental

The experimental set-up is characterized by a polymer storage bath with two air inlets, a high voltage power supply (Gamma High Voltage Research, XRM30P), and a flat grounded copper collector. The polymer storage bath consisted of the inner and outer chambers, which contained different polymer solu-

tions. A metal electrode extended from the top of the polymer storage bath in both chambers to ensure that the same voltage was applied to both solutions during the co-electrospinning process. We used also a simple arrangement of a syringe-in-syringe set-up using just one inner electrode. The inner syringe (1 or 2 mL volume) equipped with a needle (diameter 0.4–0.5 mm) was placed in the outer syringe (10–20 mL volume) equipped with a needle (diameter 0.8–0.9 mm). The needle of the inner syringe was coaxially placed in the needle of the outer syringe. The syringe assembly was positioned in a vertical set-up. A counter electrode was placed opposite to the tip of the needle of the outer syringe and an electric field was applied at high voltage (1–20 kV). In addition to the electric pulling forces, polymer solutions were also slightly pressurized to achieve a more stable co-electrospinning process (cf., Fig. 2). For example, in the case of PEO–PEO solutions the inlet air pressure in the inner chamber was kept at 90 mbar, and in the outer chamber at 20 mbar.

Nanofibers obtained were analyzed, using an optical microscope (Olympus BX51 system microscope ( $\times 1000$ ) fitted with a DP12 digital camera), as well as by a TEM (JEM 2010 and JEM 3010 apparatus) operated at 300 kV.

To prepare PEO–PEO fibers, PEO of  $M_w = 6 \times 10^5$  and  $10^6$  were used (Aldrich). Bromophenole (Acros) was added to the solutions of PEO only after all the PEO was dissolved. The solution compositions were 2 wt.-% PEO ( $M_w = 10^6$ ) in water/ethanol (6:4) with 2 wt.-% bromophenole (yellow), 2 wt.-% PEO ( $M_w = 10^6$ ) in water/ethanol (6:4) with 0.2 wt.-% bromophenole (blue), 3 wt.-% PEO ( $M_w = 6 \times 10^5$ ) in water/ethanol (6:4) with 0.2 wt.-% bromophenole (blue), 3 wt.-% PEO ( $M_w = 6 \times 10^5$ ) in water/ethanol (6:4) with 1 wt.-% bromophenole (yellow). A voltage of 3 to 5 kV was applied resulting in a field strength between the polymer storage bath and the counter electrode of about 0.2 to 0.3 kV cm<sup>-1</sup>.

To prepare two-component core–shell fibers, the outer syringe was filled with a 2 wt.-% PEO (Aldrich,  $M_w = 3 \times 10^5$ ) in chloroform or a 3 wt.-% solution of PLA (Boehringer Ingelheim) in dichloromethane. The inner syringe was filled with 1 wt.-% solutions of PDT (prepared by oxidative polymerization of dodecylthiophene ( $M_n = 10000$ ) [21] or 5 wt.-% Pd(OAc)<sub>2</sub>). A voltage of 38 kV was applied resulting in a field strength of about 3.8 kV cm<sup>-1</sup>.

In another experiment performed, the outer polymer solution was 3 wt.-% PEO ( $M_w = 10^6$ ) in water/ethanol (6:4) and the inner one 8 wt.-% PSU (Aldrich,  $M_w = 67000$ ) in chloroform. A voltage of 9 kV was applied resulting in a field strength of about 0.6 kV cm<sup>-1</sup>.

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## Ordered Mesoporous Niobium Oxide Film: A Novel Matrix for Assembling Functional Proteins for Bioelectrochemical Applications\*\*

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The construction of materials with tailored textures is regarded as a key step toward novel technologies. During the past decade, research on non-siliceous mesostructured materials has sparked wonderful contributions, probably due to their potentially valuable applications in areas, such as catalysis, sensors, semiconductors, and photonic and electronic micro-devices.<sup>[1–4]</sup>

Modifying electrode surfaces while retaining the high activity of the immobilized biomolecules and making feasible the direct electron transfer of the redox protein is highly desirable. Several nanoporous metal oxide films, such as titanium oxide<sup>[5]</sup> and zinc oxide<sup>[6]</sup> films, have been investigated in fundamental studies of protein–electrode interactions and the development of biosensing devices. Recently, the accumulation and reactivity of cytochrome c (Cyt-c) in nanofilm deposits of TiO<sub>2</sub> phytates has been reported by McKenzie and Marken.<sup>[7]</sup> To date, all nanoporous metal oxide substrates have

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