

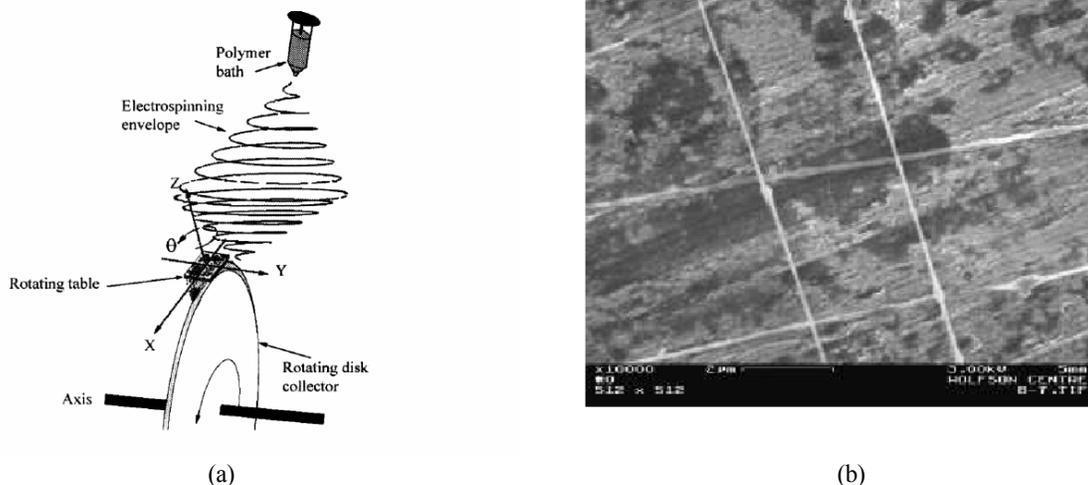
## ELECTROSPINNING OF NANOFIBERS FROM POLYMER SOLUTIONS

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**Summary** A straightforward, cheap and unique method to produce novel fibers with diameter in the range of 100 nm and even less, is related to electrospinning. For this goal polymer solutions, liquid crystals, suspensions of solid particles and emulsions are electrospun by a field of about 1 kV/cm. The electric force results in an electrically charged jet of polymer solution outflowing from a droplet tip. After the jet flows away from the droplet in a nearly straight line, it bends into a complex path and other changes in shape occur, during which electrical forces stretch and thin it by very large ratios. After the solvent evaporates, solidified nanofibers are left. The present work deals with the mechanism and electrohydrodynamic modeling, experimental realization and a number of applications. In particular, we developed a unique electrostatic field-assisted assembly technique with the aim to position and align individual conducting and light-emitting nanofibers in arrays, crossbars and ropes. These structures are of potential interest in development of novel polymer-based light-emitting diodes, diodes, transistors, photonic crystals and flexible photocells. We also discuss our experiments on electrospinning of nanofibers reinforced by carbon nanotubes, and on coelectrospinning, which yields core-shell nanofibers and nanotubes.

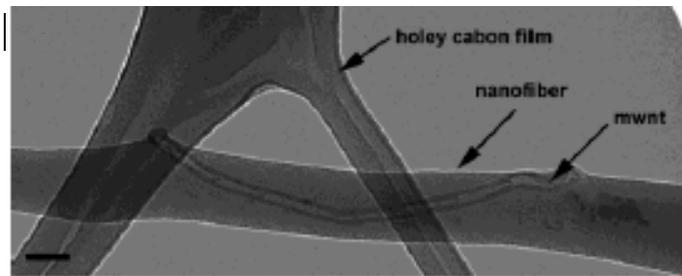
The reasons for the observed bending instability are explained and the process modelled. Several novel approaches in the electrospinning technique are introduced. In particular, to overcome technological challenges in fabrication of microdevices, techniques for in situ alignment of as-spun nanofibers/nanotubes using electrostatic repulsion forces are demonstrated as a route for alignment of nanofibers/nanotubes. A sketch of the experimental apparatus is shown in Fig. 1a.



**Fig. 1** (a) Schematic drawing of the electrospinning process, showing the double-cone envelope of the jet. The collector disk is equipped with a table that assists to collect the nanofibers. The table can be rotated about the Z-axis when the disk rotation is temporarily stopped to enable layer-by-layer collection at a desired angle between the nanofiber array layers, (b) Typical SEM image of the crossed arrays of PEO-based nanofibers collected on an aluminum table.

The jet flows downward from the surface of a pendant drop of polymer solution toward a rotating disk with a tapered edge in order to create a stronger converging electrostatic field (an electrostatic lens). During the electrospinning process, the disk was rotated at a constant speed to collect the developing nanofibers onto its sharp edge, or onto a small plate positioned at the edge. Two- and three-dimensional (crossbars) nanofiber arrays were produced by this method, Fig. 1b. Nanoropes of nanofibers are also easily doable. Arrays similar to those shown in Fig. 1b represent themselves as key elements of light-emitting diodes (LEDs), polymer lasers, and photonic crystals - a composite of a periodic array of dielectric scatterers in a homogeneous dielectric matrix. These devices affect the properties of a photon similar to a semiconductor effect on the properties of an electron. As a result, photons can have band structures, localized defect modes and surface modes. A foreseen ability to mold and guide light can enable a variety of novel applications of nanofibers/nanotubes in such fields as microelectronics, telecommunications and solar energy conversion.

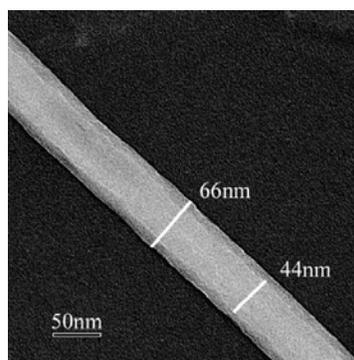
The electrospinning process was also used successfully to fabricate nanofibers of poly(ethylene oxide) [PEO] in which multiwalled carbon nanotubes (MWCNT) are embedded. Initial dispersion of MWCNTs in water was achieved using amphiphiles, either as small molecules (sodium dodecyl sulfate - SDS) or as a high molecular weight, highly branched polymer (Gum Arabic). These dispersions provided separation of the MWCNTs and their individual incorporation into the PEO nanofibers by subsequent electrospinning. The focus of this work is on the development of axial orientations in these multi-component nanofibers. Continuous nanofibers of controlled diameter were thus obtained either as an unoriented mat on a flat collector or as an oriented rope by deposition on a rotating wheel.



**Fig 2:** Oriented MWCNT in MWCNTs/PEO/SDS nanofiber. Bar=50 nm.

TEM images of nanofibers containing MWCNTs/PEO/SDS are shown in Fig. 2. It is evident that individual MWCNTs were successfully embedded in the dispersing polymer/surfactant matrix. This indicates that the original dispersion contained individual nanotubes rather than aggregates or bundles. In many regions of the electrospun nanofibers the embedded nanotubes appeared to be well-oriented along the fiber axis. Polymer nanofibers reinforced by an embedded oriented system of carbon nanotubes will allow development of advanced materials possessing ultimate tensile strength and significant electric conductivity.

A core-shell nano/meso fibers were produced by coelectrospinning of two materials. In the present approach both liquids outflowing from the core- and the surrounding concentric annular nozzles are polymer solutions or a combination of polymer solution and a non-polymeric liquid or even a powder. 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. Compound nanofibers electrospun from PEO/PSU solutions had an outer diameter of the order of 60 nm, and a core diameter of about 40nm as apparent from Fig. 3.



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

Thicker fibers (of the order of 800 nm) were also obtained, however TEM studies did not succeed in revealing their inner structure. The compound nanofiber shown in Fig. 3 demonstrates a relatively smooth core/shell interface. The method of co-electrospinning should be very versatile for the processing of a wide variety of systems 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 one. Co-electrospinning should be followed by a selective removal of the core material in the compound fiber via selective solvents or heat treatment. The preparation of organic, inorganic materials, of semiconductor systems which are functionalized via a structuring process taking place on the submicrometer scale is the main goal of the coelectrospinning process described here. The manufacturing of structured yet compact polymer fibers with diameters in the sub-micrometer range down to ten nanometers meets with considerable interest for various applications. Examples in case 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 nm-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.