Fabrication of structured micro and nanofibers by coaxial electrospinning

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Abstract. Among the different ways of synthesizing fiber and tubular micro and nanostructures, some top-down methods resort to electro-hydrodynamic forces to smoothly stretch liquids interfaces down to such small size scales. The well-known electrospinning technique, commonly used to fabricate micro and nanofibers of a broad variety of materials, is now expanded to fabricate coaxial fibers upon the generation of electrified coaxial jets instead of single jets. We briefly report different types of micro and nano structures that may be fabricated with this new technique termed co-electrospinning.

1. Introduction

Fiber-like micro and nano structures are commonly encountered in Nature. For instance, the extracellular matrix (ECM), a natural scaffold for cell, tissue, and organ growth, presents a three-dimensional (3D) structure, with defined shapes and complex porous architecture, whose topology plays an important role in cell differentiation [1]. Hollow fibers, or tubular structures, are common too, such as in feathers of birds (reduce weight and serve as heat-shields from intense solar radiation), the pelts of some polar species (e.g., polar bear), and in tiny blood vessels among many others [2]. There is a design challenge to fabricate biomaterials with such fiber-like and tubular structures in the micron and submicron size range. On the other hand, there are many technological applications in which, aside of the chemical composition and nature of the materials involved, their structure at the micron or nanometric level is also essential for obtaining outstanding performances. In this scenario, micrometric and nanometric particles with complex inner structures are thought of as ideal for many specific applications such as encapsulation [3], catalysis [4], reinforcement of materials [5], and many more.
Among the variety of methods to synthesize fibers, the electrospinning has revealed itself as a very simple method to form micro and nanofibers from liquid solutions of a broad variety of materials [6]. When a drop of liquid is exposed to an intense electric field, the net force balance on its surface re-shapes the drop into a conical meniscus, known as the Taylor's cone, from whose vertex a micro or nano electrified jet is emitted. This electrified liquid jet is stretched by the action of the electrical forces as it proceeds downstream. If, for instance, the liquid is made of a polymeric solution, then its rheology can prevent the break up of the charged jet into droplets, thus leading to the formation of micro or nanofibers of the polymer once the solvent evaporates from the jet. The same process may be applied to melt materials: as the jet cools down, it solidifies leading to the formation of fibers. The electrospinning has been extensively used to obtain mats of micro and nanofibers of a rather broad variety of materials, both organic and inorganic, or blends [7-9].

Recently, to synthesize tubular or core-shell (cable-like) structures, the electro-hydrodynamic (EHD) spinning has been extended to generate electrified coaxial jets [10] emerging from the tip of electrified conical menisci of two co-flowing liquids, in a process so-called coaxial electrospinning or co-electrospinning [11-15]. In contrast to other multi-step template based procedures, the EHD methodology is much more simple and general since, firstly, a solid template is needless and, secondly, the process is seldom affected by the chemistry of the liquids. This gentle process allows selecting the liquid precursors depending on the application or activity sought for the nanofibers.

In this co-electrospinning, two immiscible liquids are injected through two capillary needles located coaxially one inside the other. One of the liquids flows through the inner needle (i.e. inner liquid) and the other liquid flows through the annular gap between the outer and the inner needle (i.e. outer liquid). The electric voltage of this two-capillary spinneret is raised with respect to a counter electrode placed several centimetres in front of the spinneret. For a suitable range of liquids flow rates and applied voltage, the two menisci at the tip of the capillary needles adopt a conical-like shape with the outer meniscus surrounding the inner one. These menisci at certain point give rise to an electrified coaxial jet. Figure 1 shows the formation of the compound conical menisci and the electrified coaxial jet upon raising the voltage. Depending on the properties of the liquids used, the downstream evolution of the electrified coaxial jet gives birth to a variety of complex structures (i.e. coaxial fibers, tubular structures, beaded fibers, etc.), some of which will be reviewed in this work.

2. Results and discussion
2.1. Coaxial and hollow fibers

When the liquids forming the electrified coaxial jet are made of materials such that their rheology allows maintaining the coaxial structure until full solidification, then the process leads to the formation of coaxial nanofibers in one step [13, 14]. Examples of such cases are shown in figure 2. In figure 2a we show a TEM picture of a coaxial nanofiber made of poly(ethylene oxide) (PEO) on the outside (shell) and a conducting polymer poly(aniline sulfonic acid) (PASA) on the inside. The molecular weight of the PEO is 900KDa and it is dissolved in water at a concentration of 5wt%. The fiber outer diameter is 160 nm, while the diameter of the inner core is of about 30 nm. Figure 2b shows a coaxial nanofiber of PEO (shell) and another polymer poly(acrylonitrile) (PAN, core). The fiber outer diameter is 170 nm and the inner core is of about 30 nm.

![Figure 2](image)

**Figure 2.** TEM images of core-shell nanofibers: (a) PEO-PASA. (b) PEO-PAN. Scale bars are 50 and 200 nm, respectively.

The usefulness of the co-electro spinning has also been extended as a method to form fibers of polymers which, by themselves, are unspinnable. Although it can also be done by adding binders (other polymers) to the one of interest, the spinning of these blends leads to fibers of the blend, but not of the “pure” polymer. Some examples include spider silk [16] or poly(ethylene glycol) for drug delivery [17] among others [18]. The process, in this case, resorts to the use of a spinnable polymer as the shell to form the coaxial fiber, thus maintaining the fiber-like shape of the core, that is, the unspinnable polymer. In some cases, such as in the silk case, there is a need for cross-linking the inner polymer before degrading or removing the outer shell (the template). Another example is alginate. This is a well known biocompatible polymer, used in a variety of biological applications [19, 20]. In this case, we have co-electrospun PEO as shell and alginate as core to form the sought coaxial nanofibers. To crosslink the alginate, we have used a solution of calcium chloride in water, where the as-collected nonwoven mat of fibers is immersed: the Ca$^{2+}$ diffuses across the PEO shell before it dissolves completely and reaches the alginate, thus provoking its cross-linking. The mat can then be flushed with water to remove the residual PEO shell, thus leaving the nanofibers of pure alginate. These four steps to obtain pure alginate nanofibers are sketched in figure 3a. An example of such fibers is shown in figures 3b (as-collected) and 3c (after cross-linking).
Figure 3. a) Sketch of the steps to obtain pure alginate nanofibers. b) PEO(shell)-Alginate(core) compound nanofibers. c) Alginate nanofibers after its cross-linking and PEO removal. Scale bars are 5 µm.

It is also possible to obtain hollow fibers in just one step through co-electrospinning if the inner liquid is non-polymeric (i.e. a regular liquid). In order to form the tubular structure, the mechanical strength of the material the hollow fibers will be made of must be strong enough to hold the cylindrical shape regardless of the mechanical stresses appearing during the spinning process. The inner liquid is used as a sacrificial core which is eliminated by diffusion through the tiny pores and failures of the wall. This approach was successfully achieved in combination with sol-gel formulations to form hollow spheres and hollow nanofibers (figure 4a) [11, 13]. Recently, other solid precursors have also been employed to synthesize hollow fibers (figure 4b) [21].

Figure 4. SEM images of hollow nanofibers made of a) TEOS (a silica precursor) as an inorganic shell and b) Lignin (a carbon precursor) as an organic shell. Both examples use glycerine as the sacrificial core. Scales bars are 1 µm and 2 µm, respectively.

In the case of many organic polymers, however, the mechanical strength is not enough to withstand the stresses, and the hollow tubular structure collapses unless the structure is stabilized. An alternative consists of synthesizing a coaxial nanofiber of the polymer of interest on the shell and a sacrificial polymer in the core; in this case, the core plays the role of a template. The whole structure may be stabilized and, if the properties of the template are appropriate, it may be degraded and
eliminated without affecting the shell, leading to a hollow fiber made of the polymer of interest. Although it is a multi-step process, the basic coaxial fiber can easily be made in just one step. Following this approach, we have fabricated hollow nanofibers of organic polymers like PAN and PVP. PAN is a precursor of carbon fibers which has been electrospun since 1996 [7]. This polymer, although very expensive, is broadly used in industry for this purpose, since its carbon yield is of about 40% to 50%. Very recently, co-electrospinning of PAN on the outside and of PMMA on the inside has resulted in the formation of coaxial fibers which, after a proper thermal treatment and carbonization, yielded hollow micron fibers of carbon [22]. The main difference is that, in our case, we used a different sacrificial polymer, poly(propylene carbonate) (PPC), which degrades at rather low temperatures (about 200°C). After collecting the coaxial electrospun microfibers, the PPC of both the shell and the core decomposes under the thermal treatment, so the tiny pores left in the shell by the PPC are used by the PPC in the core to escape, thus yielding a porous hollow fiber of stabilized PAN, which after carbonization became porous hollow carbon fibers. The final fiber diameter is of the order of 0.9 microns, whereas the shell thickness is about 200 nanometers.

We have also co-electrospun a blend of PVP-PPC (shell) and PPC (core), both in DMF, to form coaxial nanofibers. After thermally treated, the PPC leaves the whole structure, leaving hollow nanofibers of stabilized PVP. Outer diameter is of the order of 700 nm, with 200 nm of wall thickness (figure 4).

![Figure 4. SEM images of hollow nanofibers of stabilized a) PVP and b) PAN. Scale bars are 1 µm and 3 µm.](image)

### 2.2. Beaded fibers

The possibility of encapsulating liquids is very attractive for many applications such as drug delivery, cosmetics, etc. The typical way for doing so resorts to emulsification of the liquid in a polymer solution, which afterwards is spun into fibers. Some examples are demonstrated [23, 24] for proteins and cells encapsulation inside hydrophobic polymers such poly(ethylene-co-vinyl acetate) (PEVA). The encapsulated liquid/cells are randomly distributed along the polymer nanofibers. Although this approach is very efficient, the use of co-electrospinning provides a further degree of control on the structure of the fibers, as recently demonstrated [25]. When the outer liquid is a polymeric solution and the inner one a regular liquid (i.e. oil, water, etc.), the downstream evolution of the electrified coaxial jet is such that the inner jet (made of a regular liquid) may break into droplets as the stretching proceeds, whereas the polymeric shell solidifies. The process is sketched in figure 5a. As a result, one obtains polymeric micro or nanofibers encapsulating the inner liquid in discrete pockets (beads). Figures 5b and 5c show pictures of the beaded fibers resulting of a co-electrospinning
of PIB (shell) and water plus paprika (a UV marker) in the core. The water is encapsulated inside the beads along the microfibers of PIB, as shown by fluorescence analysis.

![Figure 5](image_url)

**Figure 5.** Images under UV light of: a) dense non-woven mat of PIB containing water beads. b) PIB microfibers encapsulating water plus paprika as a UV marker. c) Evolution schema from the coaxial electrified jets to the beaded fibers.

Interestingly, both the bead diameter and the bead-to-bead distance are rather uniform and may be varied by controlling the fluids flow rates, thus providing an extra degree of control on the structure. This approach is being extended to other liquids, including liquid crystals. The external control over the refractive index of these materials could allow generation of switchable 1D diffraction gratings, analogous to the 2D and 3D structures recently reported [26, 27].

To end this section, we describe some experiments that we have carried out to trap or encapsulate in fibers particles that may change their dimensions in response to the adequate external stimuli. For this example we have used monodispersed microgels of N-isopropylacrylamide co-polymerized with acrylic acid as the active particles. These microgels are spherical monodisperse particles of colloidally stable hydrogels that can notably change their diameter from ~0.4 to ~3.0 microns, depending on the pH [28] and on the temperature [29] of the liquid phase in which they are suspended, as schematically shown in Figure 6a. The diameter of the dry microgel is of about 400 nm as shown in figure 6b.

![Figure 6](image_url)

**Figure 6.** a) Microgel response in water at different pHs and temperatures. b) TEM image of the dry microgels. Scale bar is 2 µm.
We have electrospun a suspension of microgels in a mixture of PVP in DMF. This suspension seems stable for a rather broad range of microgel loading, from 1 to 40 % in mass. The electrospun fibers consist of beads containing several microgels randomly distributed along the nanofibers of PVP. The fibers are thermally treated to crosslink the PVP, so the mat may now be put in water at different pHs and/or temperature. Since the PVP is crosslinked the mat does not dissolve and the microgels remain trapped inside it. However, the water can flow in and out through the PVP shell due to its permeability. Figures 7a and 7b show optical images of the same piece of fiber immersed in water at room temperature for two different pHs. The change in size of the microgels is clearly visible between the two images, indicating that they remain active after the electrospinning process and even after the gentle thermal treatment. The macroscopic appearance of the mat after thermal stabilization is presented in figure 7c.

![Optical micrographs of microgels trapped inside PVP nanofibers: a) swollen response after immersing the nanofibers in a basic solution and b) shrink response after drying them at 45°C for 20 seconds. c) Macroscopic appearance of the mat after thermal stabilization. Scale bar is 2 cm.](image)

**Figure 7.** Optical micrographs of microgels trapped inside PVP nanofibers: a) swollen response after immersing the nanofibers in a basic solution and b) shrink response after drying them at 45°C for 20 seconds. c) Macroscopic appearance of the mat after thermal stabilization. Scale bar is 2 cm.

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