Electrically Forced Coaxial Nanojets for One-Step Hollow Nanofiber Design

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New materials with tubular shapes and characteristic lengths below one micrometer have recently been proposed to develop novel field emitter displays and magnetic media,1 controlled-release,2 and adsorbent3 materials among many others. These tubular (as well as similar rodlike) inorganic and organic—inorganic structures, which differ from the popular carbon nanotubes,5,6 are still made via multistep approaches.7−14

There is ample choice as to the type of chemical precursors and synthetic approach to produce non-carbon nanotubes.7−9,11−14 However, strategies almost inevitably fall into two general categories: the so-called template method, and molecular self-assembly. Template methods have arguably constituted the simplest and most effective way to prepare these nanostructures, despite the fact that they often present problems. First, chemical or physical adherence onto the surface of the template depends on case-specific interactions i.e., a particular approach may not even be adaptable to the synthesis of a chemically similar material. Second, the first synthetic step is the design of a nanotemplate, which is not necessarily a trivial task. In addition, the use of solid templates invariably leads to a multistep approach: template design, growth of the structure on or around the template, and ultimately its selective removal from the precursor (composite) structure. Thus, much of the complexity of template and self-assembly methods comes from the need to rationally design either solid- or liquid-crystal-type template nanostructures via specific chemical processes and from their multistep nature.

In this communication, we demonstrate for the first time the capabilities of electrohydrodynamically (EHD) generated coaxial liquid jets15,16 combined with sol−gel chemistry17 to produce hollow nanofibers in a single step. The novelty lies in that coaxial two-liquid nanosols are made of a shell-forming liquid on the outside and an inert immiscible (or poorly miscible) liquid on the inside, the latter constituting a very broad and general family of liquid nanotubular templates requiring no molecular-level assembly. Gelation of the sol (shell) constituent prior to electrical charge-mediated breakup of the coaxial nanojet yields hollow nanofibers having a liquid-filled core (i.e., the liquid template), which evaporates on collection. This simple process yields hollow nanofibers in a straightforward manner. The technique can readily be extended to other chemical systems that afford electrospinning processing.18

Electrohydrodynamic (EHD) forces provide a method to produce submicrometric liquid jets from a nozzle much larger in diameter than the jet itself. A liquid meniscus exiting the tip of a capillary, when subject to an appropriate electric field, deforms into a conical shape (Taylor cone), from whose tip a slender micro- or nanojet is issued. The natural fate of the jet is generally to break up into a spray of highly charged nanodroplets, fittingly known as an “electrospray”,19−22 unless the jet solidifies before such physically natural disruption occurs. In the latter case, the EHD process has been successfully applied to produce nanofibers in a technique termed electrospinning: solidification of the liquid thread occurs while it is still in its cylindrical, metastable form.

Recent work in which (EHD) forces are used to produce highly charged, compound Taylor cones and submicrometric jets of two immiscible (or poorly miscible) liquids provides the key to devising such a general nanotube production method.15−17 The experiment is sketched in Figure 1. Two coaxial capillary tips are used to simultaneously feed the two liquids. At a short distance from this two-capillary nozzle, typically several centimeters, a metallic plate is placed as counter-electrode or collector.

Liquid-in-liquid nanodroplets, as well as solid capsules with a well-defined core—shell structure have just been made.15−17 The capsules were formed as a consequence of the varicose break-up of the coaxial jet taking place before the gelation of the outer liquid. Regardless of whether one is seeking capsule or hollow fiber production, there is a priori no requirement for favorable chemical or physical adherence between the shell-forming fluid and a molecularly disorganized liquid template. To the best of our knowledge this represents the least specific scenario for nanotube engineering. Providing the shell withstands capillary forces on liquid core removal, the method is also much less tedious than those requiring removal of a solid template. If the solidification (or gelation, polymerization, etc.) time of the outer liquid is smaller than the residence time of that liquid within the coaxial jet, fibers are indeed obtained. In the example shown below, the liquid flowing
on the outside was a formulation based on an aged sol of tetraethyl orthosilicate (TEOS). Its viscosity and electrical conductivity are fine-tuned by aging (hydrolysis followed by polycondensation of TEOS) and composition, so that the gelation rates during the EHD process may be varied. As inner nanojet templates, we have successfully used innocuous liquids such as olive oil (as purchased) and glycerin (Panreac) without further purification. Due to the electrical conductivity of the aged sol (in the order of $10^{-2}$ S/m), which is much larger than those of the liquid templates employed in this study, the diameter of the jet is submicrometric. To avoid deviations from cylindrical shape, the gelation-to-jet perturbations growth time ratio must be decreased as much as possible. In our scheme, this can be accomplished by either decreasing the gelation time via an increase of the pre-EHD aging times or by increasing the perturbation growth time. It is known that the growth rate of capillary deformations depends on the properties of the liquids, primarily surface tensions ($\gamma$) and viscosities ($\mu$). More stable and therefore longer jets are favored when $\gamma$ is reduced and $\mu$ is increased. These two properties, along with electrical conductivity, determine the ability of our process to make extremely small and uniform nanotubes. While control of operating variables such as flow rates (core:shell volumetric flow ratio) and voltage is an important aspect of the process, the physical properties of the liquids also play a key role in determining the ultimate diameter of the fiber or liquid nanotube precursor.

A SEM image of as-collected hollow silica-based fibers is shown in Figure 2A. Figure 2B shows the same fibers after being transversally cut to expose their tubular structure, which shows diameters in the order of 500 nm and an average shell thickness of about 70 nm. The relatively good degree of monodispersity in the diameter of the fibers seems to indicate that jet-splaying instability is absent, probably because the electrical charge level on the jet is relatively moderate. A magnified view of one of these fibers is shown in Figure 2C. In Figure 2D we show a bundle of fibers collected within just a few minutes of EHD processing. The tubular structure is preserved on drying at 500 °C.

Besides its simplicity, another advantage of the process is that control of both wall thickness and fiber diameter is a relatively simple task, since core and shell liquid flow rates and applied voltage can be independently controlled. We have also elected to use a nontoxic liquids as nanotube templates since such processing fluids are likely to enjoy popularity among readers with an interest in commercial nanotube manufacturing. A natural extension of this work is the use of dissolved polymers as core liquids to make sheathed fibers.

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**Supporting Information Available:** Experimental descriptions and hydrous zirconia nanotube preparation. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

**References**


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