Developments in electrohydrodynamic forming: Fabricating nanomaterials from charged liquids via electrospinning and electrospraying

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Although centuries old, electrospinning stands out as one of the most useful and flexible techniques for producing nanomaterials. Parallel to the burst of enthusiasm in nanomaterials in recent years, interest in electrospinning has surged exponentially over the past decade as theoretical advances in ceramics and other materials components have grown. As a result of improvements in electrospinning modeling, processing, measuring and testing, new applications are emerging that range from health care to high-temperature and high-pressure filtration, as well as new routes to explore and control crystal growth. Herein, our authors from the University of Florida describe the history of, and current trends in, electrospun materials.

Electrospinning is the process of using an electrical charge to pull a very thin fiber from a liquid. Electrospinning and the related process of electrospraying comprise the larger field known as electrohydrodynamic forming. Electrospraying is the formation of nanoparticles, and electrospinning describes the fabrication of long fibrous structures. Both processes transform liquid droplets into nanomaterials through strong electric fields that are on the order of several kilovolts per centimeter.

These processes deserve attention by ceramists and other materials researchers, because recent insights into electrohydrodynamic phenomena have led to the fabrication of long nanofibers, core-shell fibers, tubes and spherical particles

Fig. 1: Electrospraying devices used for entertainment purposes. Published in Essai Sur L' El électricité Des Corps in 1746.

with dimensions less than 100 nanometers. These advances are instilling new spirit into a field that started more than four centuries ago.

The particular interest in electrospinning results from its versatility. Researchers using this technique are able to create nanofibers and nanotubes from almost any soluble polymer and a wide range of ceramic and composite systems. Furthermore, reduction of ceramics even allows the formation of metallic nanofibers. Fiber diameters can range from tens of nanometers to several micrometers. Another salient characteristic of electrospun fibers is their enormous aspect ratios: The fibers can reach several meters in length while maintaining nanometer-scale diameters. Electrospinning also provides investigators a distinctive ability to control fiber orientation, porosity and morphology.

Historical observations and early developments

For hundreds of years, seafarers have reported ominous glowing lights on the masts of their ships during electrical storms. Some sailors believed the light to be a good omen and often referred to the glow as "St. Elmo's fire."

In reality, the conditions that caused this glow were a warning that lightning was likely to strike at any moment. An electric field concentrated at the tip of the mast and ionized the surrounding air molecules to create the ethereal glow.[1]

A less obvious electrohydrodynamic phenomenon is that as rain falls into an electric field, the field introduces a new force to the droplets, one that is strong enough to change their shape and that may even cause electrospraying.

At least one early scientist took notice of this effect on liquids. William Gilbert first recorded the curious behavior of liquid droplets in electric fields around 1600.[2] Gilbert devised several experiments to demonstrate the distinct behaviors of electricity and magnetism. His observations were published in his work, *De Magnete*. Using charged amber, he was able to deform the shape of water droplets without physical contact. This description started the study of electrohydrodynamics. Although the practical applications of this phenomenon were not immediately realized, demonstrations of its effects were used to entertain (Figure 1). Despite Gilbert's work, the next known publication related to this field did not appear until 1882, when Lord Rayleigh published a theoretical model that describes electrical forces needed to cause droplets to eject liquid.[3]

In the 1960s, Sir Geoffrey Taylor became the first to undertake a rigorous theoretical study on charged liquid droplets. Taylor observed how droplets under an electric field could deform into a new equilibrium shape that resembled a cone.[2,4] These so-called Taylor cones emitted fluid from their tip. He discovered that the ejected fluid could exhibit two distinctive behaviors, either forming discrete droplets that travel directly to the counterelectrode plate or forming long strands of liquid that whip around before reaching the electrode.[5]

An important breakthrough to this field occurred when researchers began incorporating polymers dissolved in volatile solvents into the electric field. As the droplets travel through the electric field, the solvent evaporates, leaving behind polymeric nanostructures.

This phenomenon does not occur with all polymers. Low-molecular-weight polymers typically form the droplets that are the signature of electrospraying. However, the rheological properties of high-molecular-weight polymers prevent the material from breaking apart into spheres. Instead, long, continuous polymer fibers are emitted.[6]

Attempts to commercialize this phenomenon began to appear in 1902, when two patents were granted that described methods to electrically disperse water droplets.[7,8] Anton Formhals was the first to lay claim to the process of electrospinning in a 1934 patent.[9] In 1936, Petryanov-Sokolov ingeniously developed one of the first applications for electrospun fibers: filtration. The underlying reasoning for Petryanov-Sokolov's innovation comes from filtration theory, which holds that thinner fibers make more efficient filter material. Indeed, industrial-scale production of these filters began shortly thereafter in the former Soviet Union.[10]

Despite Petryanov-Sokolov's breakthrough, intensive and detailed study into the behavior of electrically charged fluids did not begin until the early 1980s.

The modern era of electrospinning

Industrial-scale electrospinning equipment can be quite complicated. However, at the laboratory scale, relatively simple setups are used to produce fibers. The essential components of a typical laboratory-scale electrospinning setup, shown in Figure 2, are an electrically charged capillary attached to an advancement pump and a grounded collection plate.

Pressure from the advancement pump causes the capillary to emit a small droplet of the viscous polymer–solvent liquid. The electric field stretches the droplet, which forms a Taylor cone, and soon accelerates an elongated strand of solution onto a grounded substrate. The solvent begins to evaporate as soon as it is emitted from the needle.

The fiber does not travel in a

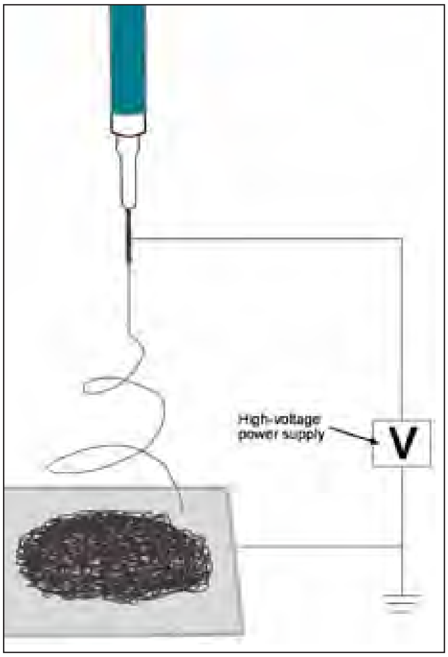

Fig. 2: Typical laboratory-scale electrospinning apparatus that allows production of milligram to gram amounts of ceramic nanofibers.

straight line. One characteristic of electrospinning is that electrostatic forces cause the material to whip around. This motion helps thin the fibers and accelerates the solvent evaporation. The end result is a collection of solid nanofibers, and in this collection-plate setup, the fibers deposit in a randomly entangled mesh. The fibers then can be separated from the substrate and used in a number of applications.

Perhaps the most interesting aspect of electrospinning is its versatility. Investigators have demonstrated that a wide range of material systems can be transformed into nanofibers. Furthermore, with additional modifications to the process, one can produce a variety of structures and morphologies. For example, small particles, salts and ceramic precursors easily can be added to the polymer–solvent solution, which is then electrospun into fibers bearing those materials. This further enhances the variety of materials that can be electrospun.[11-15] Researchers have shown that the polymer–solvent is not always a requirement by electrospinning polymerless sol–gel systems.[16]

Postelectrospinning steps often are necessary to modify the final electrospun fibers. Heat treatments can be used to carbonize polymer fibers or burn out the polymer material to form entirely ceramic fibers.[17] Although the vast majority of electrospinning research is focused on polymeric and ceramic materials, investigators also have demonstrated that ceramic fibers can be reduced to form metallic fibers.[18] Another study has utilized electrospun fibers as templates for forming metallic nanotubes.[19]

Additional modifications to the electrospinning setup have led to a diverse collection of unique nanostructures. In 2003, Sun et al.[20] demonstrated that separate polymer solutions could be pumped into different compartments of concentric capillaries to electrospin core-shell fibers. A year later, Li et al.[21,22] produced hollow fibers by replacing the inner capillary fluid with heavy mineral oil, which was extracted after electrospinning.

Although the classic electrospinning approach produces fibers collected in a randomly oriented nonwoven mat, several research teams have developed modified collector setups that orient fibers along a single axis to produce aligned nanofibers.[14,23–29] In fact, we now know that there is a useful variety of morphologies that are possible with electrospun fibers (Figure 3).

Theoretical developments

Numerous models exist that describe the electrospinning and electrospraying processes. A series of papers, published by Hohman and Shin[31–33] in 2000 describes the whipping motion of electrospun jets. Instabilities in the electric field cause the fiber to whip around. A refinement of the analysis was subsequently published by Feng.[34]

Obtaining very thin fibers is of paramount importance for many electrospun applications. To this end, theoretical models were developed to determine how various electrospinning parameters affect the final fiber diameter. Fridrikh et al.[35] proposed a model to predict the final fiber diameter of electrospun systems. They used their model to achieve an accuracy of around 10 percent for a poly(ethylene oxide) system. (Several numerical approaches also have been used to model the electrospraying process, which are summarized in several reviews.[36,37])

High conductivity in ceramic sys-

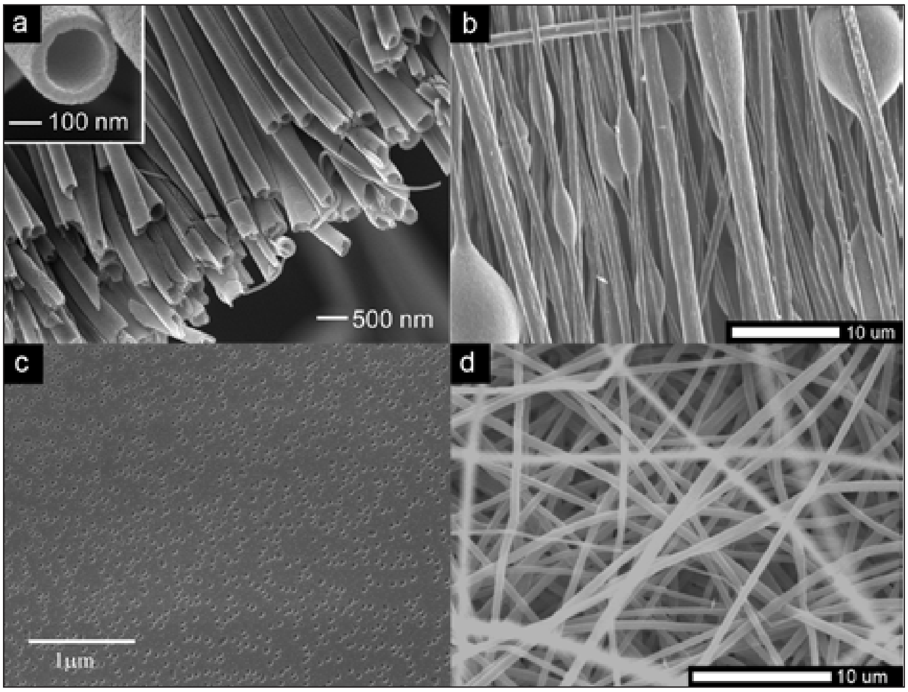

Fig. 3: (a) Hollow, aligned electrospun fibers; (b) Beaded, aligned polystyrene fibers; (c) Porous surface of a polystyrene fiber; and (d) Random mesh of TiO_2 fibers. (a) and (c) reprinted with permission from References 21 and 30, respectively. Copyrights 2004 and 2002, American Chemical Society.

tems invalidates several of the assumptions presented in previous models. To accommodate for the higher conductivities of these systems, Sigmund et al.[13] proposed a model for ceramic systems. These equations act as guides for determining which parameters have the greatest impact on the final fiber diameter. However, they have limitations. The equations assume all materials can be electrospun and that the fibers are continuous and uniform. In practice, some materials cannot be electrospun. Furthermore, certain conditions not accounted for in the equations result in nonuniform fibers because of the formation of beads and pores within the strands (Figures 3(b) and 3(c)).[38–41]

Experimental developments

Our current research encompasses several areas in electrospinning with a particular focus on advancing the theoretical understanding and processing of ceramic nanofibers. Central to this pursuit is improving the properties of ceramic fibers, which are typically polycrystalline and brittle. Often, nanofibers fracture during heat treatment or shatter when handled. To improve the practical applications of ceramic fibers, our research group has conducted several studies to overcome these hurdles. One achievement is that we established a three-point bending technique using atomic force microscopy to measure the mechanical properties of individual ceramic nanofibers.[42]

Later developments have led to ceramic nanofibers of sufficient strength for filtration purposes. These fibers are easily handled after the sintering process. Because of their strength and chemical stability, these fibers may be of particular interest to filtration applications where extreme conditions may be encountered.[43]

Ceramic nanofibers offer interesting opportunities to control crystal growth. Grain growth in nanofibers is hindered by their 2D structures so that grain sizes in electrospun fibers are typically smaller than those produced by other processing methods.[44] Small grains improve many ceramic properties. Therefore, there also is a great interest in synthesizing single-crystal fibers. This is a challenge that could improve their electrical, mechanical and optical properties. Yuh et al.[45] synthesized single-crystal fibers composed of $BaTiO_3$ by carefully controlling the processing conditions. These fibers also represent the first complex oxide electrospun ferroelectric structures.

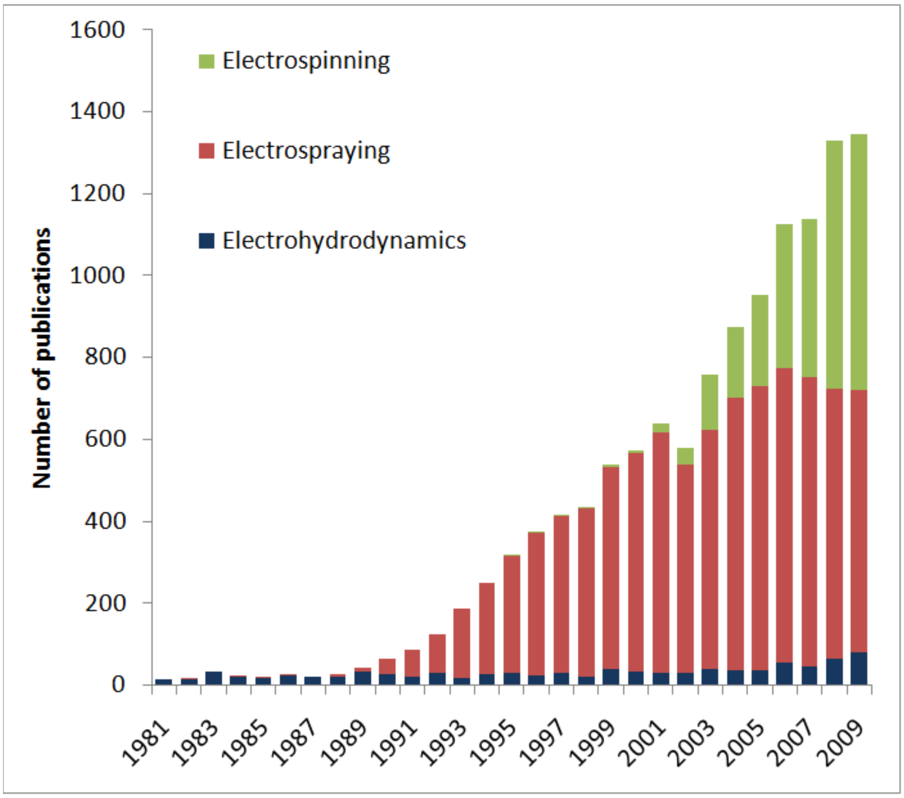

Fig. 4: Electrohydrodynamic publications based on a search of publication titles in ISI Web of Knowledge in October 2010. Incomplete data for 2010 were not included in the chart.

Growing applications

As noted earlier, one of the predominant applications of electrospun fibers is in filtration systems. Improvements continue to be made in this field as various types of fibers are studied, and techniques to upscale the electrospinning process are developed.[10]

However, electrospinning is not limited to filtration: It is applied to several disparate fields. For example, the ability to process biocompatible fibers from nonhazardous solvents is of interest to a variety of biomedical applications, such as scaffolds for cell growth. Numerous studies also demonstrate the usefulness of fibers for wound healing and tissue engineering.[46–48] Energy applications, such as solar cells, batteries, capacitors and fuel cells, also have made use of electrospun fibers.[11,49]

The ability to produce fibers from such a vast range of materials ensures that the number of new applications will not be exhausted anytime soon.

Publishing trends and outlook

The trend of publications in the field of electrohydrodynamics is impressive (Figure 4). A surge of electrospraying publications began in 1988. The earliest publication to use the term “electrospinning” appeared in 1995. Since then, publications in electrospinning have greatly increased each year.

These articles cover a wide range of topics, including theoretical developments, novel processing techniques, development of new materials and composites and new applications. The greatest number of papers published related to electrospinning fall in the biomedical field, with a particular emphasis on scaffolds. The next most common areas are energy storage and conversion, filtration and catalysis.

Credit: M.J. Laudenslager and W.M. Sigmund.

Electrospinning droplet deformation.

Interest in electrospinning continues to gain momentum. Processing innovations are expanding the range of morphologies and production quantities of fibers. The variety of materials that can be electrospun opens the technique to many avenues of research, many of which remain undiscovered.

Methods to improve the production capacity of electrospun fibers are an ongoing development by several companies. Innovative techniques have radically altered the electrospinning setup to make use of multiheaded jets and needleless systems. However, consistently producing large quantities (tons) of fibers remains the greatest challenge to the industrial use of the process. ■

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Electrospinning and electrospraying: Turning up the volume

Electrospraying and electrospinning have proved to be valuable methods for custom and small-volume applications. However, as Laudenslager and Sigmund note, finding high-volume electrodynamic processes is a challenge to engineers and manufacturers.

The building of high-throughput systems and equipment capable of producing well-controlled and narrow particle- or fiber-sized distributions at massive rates is not easy because there is not a universal or unique solution in terms of device geometry and device parametric operating range. The Taylor cone must undergo dynamic processes that can be dramatically different in each application. The process depends on the type of particles or fibers to be produced and on the substances and materials involved in the particle- or fiber-formation process.

A trustable upscaling of production must start from the study and characterization of the most basic setup: the single-needle electrospray or electrospinning process. Once the basic characterization of the materials, solvents and equipment has been established, there is plenty of room to innovate and reach higher volumes. Two particularly intriguing methods are multi-needle (multinozzle) processes and – even more extreme – needleless processes, as exemplified by the commercial work of Yflow and Elmarco, respectively.

Fifty nozzles are better than one

Yflow (www.yflow.com) was founded in 2001 by scientists from the Universities of Málaga and Seville in Spain and has since developed outstanding know-how in using devices with heads that contain scores of nozzles to create nanofibers, coaxial fibers, hollow capsules and filled capsules.

Yflow says that, once the single-needle formation process is properly characterized, it then tests a multinozzle piece. This is a “first-order upscaling,” where the objective is to increase the particle or fiber yield by one or two orders of magnitude. The reason for this step is that, when separate single-needle processes are brought close to each other, Yflow typically sees the particles or fibers exhibit a strong interaction among themselves, This may deteriorate the quality of the particles/fibers as well as break down the whole process. Again, such interaction strongly depends on the physical and chemical properties of the fluids as well as on the geometry of the multinozzle piece. The optimization of the first-upscaling step allows operators to define an initial “building block.”

In the next step, the objective is to increase the particle/fiber yield by three or four orders of magnitude. Here, the initial building block is repeated and integrated in a basic upscaling modulus. Yflow says that, even though the design has been optimized to produce a specific material, the modulus then can be readjusted easily to yield various types of particles or fibers by substituting other multinozzle pieces that have been optimized for a different type of material. Similar adjustments can be made to produce the same materials but in various sizes.

Yflow’s approach to increasing volume is to use arrays of multi-nozzle modules.

The actual modules are intended to operate as completely independent units, such that no “cross-talking” occurs when several are placed next to each other. Thus, the final level of production required by a customer may be supplied by grouping as many of those modules as needed. An additional benefit of this modular scheme is that it allows much easier maintenance of the units.

Another essential aspect of the mass production is the collection system for the particles or fibers. Some Yflow customers are seeking nonwoven mats of nanofibers that will be applied later on certain substrates or be subjected to postprocessing. In some cases, a conveyor-type collector works well. However, there are situations in which the fibers must land on specific substrates in such a way that the multinozzle module must move in a certain fashion above the substrates.

For other applications, the desired product is spheres (capsules, for instance). Depending on the materials they are made of, the capsules may be tremendously sticky. In these scenarios, special care must be taken to select the collector material in order to efficiently remove the microcapsules or nanocapsules afterward. For certain applications, the capsules might need to be postprocessed before they gain mechanical rigidity (such as in the case of liquid capsules). Therefore, collection must be performed in a liquid collector instead of a solid one.

No needles are better than one

The Czech Republic-based Elmarco (www.elmarco.com) makes use of a discovery by which it is possible to produce Taylor cones and material flows from a tip of a needle or nozzle or from a thin film of polymer solution. In its patented Nanospider nozzleless process, multiple fiber “jets” form spontaneously from a thin film, which is carried on the surface of a rotating drum, when the drum is exposed to a high-voltage electric field of a critical value.

The number and location of the jets spread out on the drum depend on a number of factors, including temperature, conductivity, liquid density, surface tension and electric-field strength. Elmarco says it avoids some of the multinozzle process steps by letting the jets set up naturally, noting, “[F]ree liquid surface electrospinning lets natural physics define this distance, rather than using individual needles. This allows higher fiber packing density and, thus, an increased productivity as well as better fiber homogeneity and more consistent web morphology.”

Elmarco says another benefit is more homogenous fiber layers. A final benefit of a nozzleless process is easier maintenance and cleanup: There are no needles or nozzles to unclog or clean.

As these examples imply, the possibilities for using electrospinning and spraying are almost as many as material combinations and applications. However, it is precisely this broad scope that prevents the upscaling from having a unique solution. ■

Elmarco’s Nanospider nozzleless process can allow a large number of jets to form naturally out of a thin film of a polymer solution.