COMMENTARY

Electrospinning spinneret: A bridge between the visible world and the invisible nanostructures

Wenliang Song,[1,2,4,*] Yunxin Tang,[1,4] Cheng Qian,[3] Bumjoon J. Kim,[2,*] Yaozu Liao,[3,*] and Deng-Guang Yu[1,*]

[1]School of Materials and Chemistry, University of Shanghai for Science and Technology, Shanghai 200093, China

[2]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[3]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

[4]These authors contributed equally

*Correspondence: wenliang@usst.edu.cn (W.S.); bumjoonkim@kaist.ac.kr (B.J.K.); yzliao@dhu.edu.cn (Y.L.); ydg017@usst.edu.cn (D.-G.Y.)

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Fabricating novel structures allows for the development of innovative technologies in nanoscience. The methods to fabricate nanomaterials can be categorized based on the key elements determining the final structures of the materials. Electrospinning exhibits unparalleled advantages in the fabrication of nanofiber-based structures by benefitting from the effective interactions between the electrostatic energy and working fluids on a spinneret. As a convergence point of fluids and energy, the structure of the spinneret nozzle plays an important role in the working process and the resulting quality of the fibrous structures.[1] The appropriate design and application of the multiple-channel spinneret can provide effective strategies to duplicate complicated structures in the visible world to the "invisible" nanoscale, which can stimulate new types of bionic approaches and promote the development of nanomaterials and nanodevices with even smaller (picotechnology), more orderly (array), and more complex structures compared with those of the existing materials.

Conventional electrospinning spinneret

Conventionally, the electrospinning spinneret is solely a single hollow metal capillary where, on its top, the spherical droplet could evolve into the Taylor cone under applied direct current or alternating current. However, conventional spinnerets often result in solid fibers with all compositions mixed in the filament-forming matrix. Although they may be exploited as templates for further fabrication, it is difficult to directly control the inner porosity, morphology, and structure of fiber materials with the single hollow syringe-based spinneret. The emerging applications in catalysis, energy storage/conversion, environmental and biomedical areas require the fiber materials to not only contain two or more types of polymer solutions but also to incorporate nonpolymeric materials such as metal oxides, ceramics, semiconductor materials, and drugs. Thus, the fibers produced by the conventional spinneret often have limited application in these areas. Along with the fast development of materials science and technology in this nano era, electrospinning faces new challenges such as accurate manipulation of the inner structures of nanofibers and their related properties. The key lies in the spinneret, which is a template for duplicating complex nanostructures from the macrostructure of its nozzle.

Bionic design of the electrospinning spinneret

Bionic design is an ancient yet contemporary discipline that has been developed based on bionics and design. Bionic design consists of imitating the unique skills of living things and designing products or solving problems using biological structures and functional principles in mechanical design. Technology transfer between life forms and manufactured objects is desirable, and using a feature

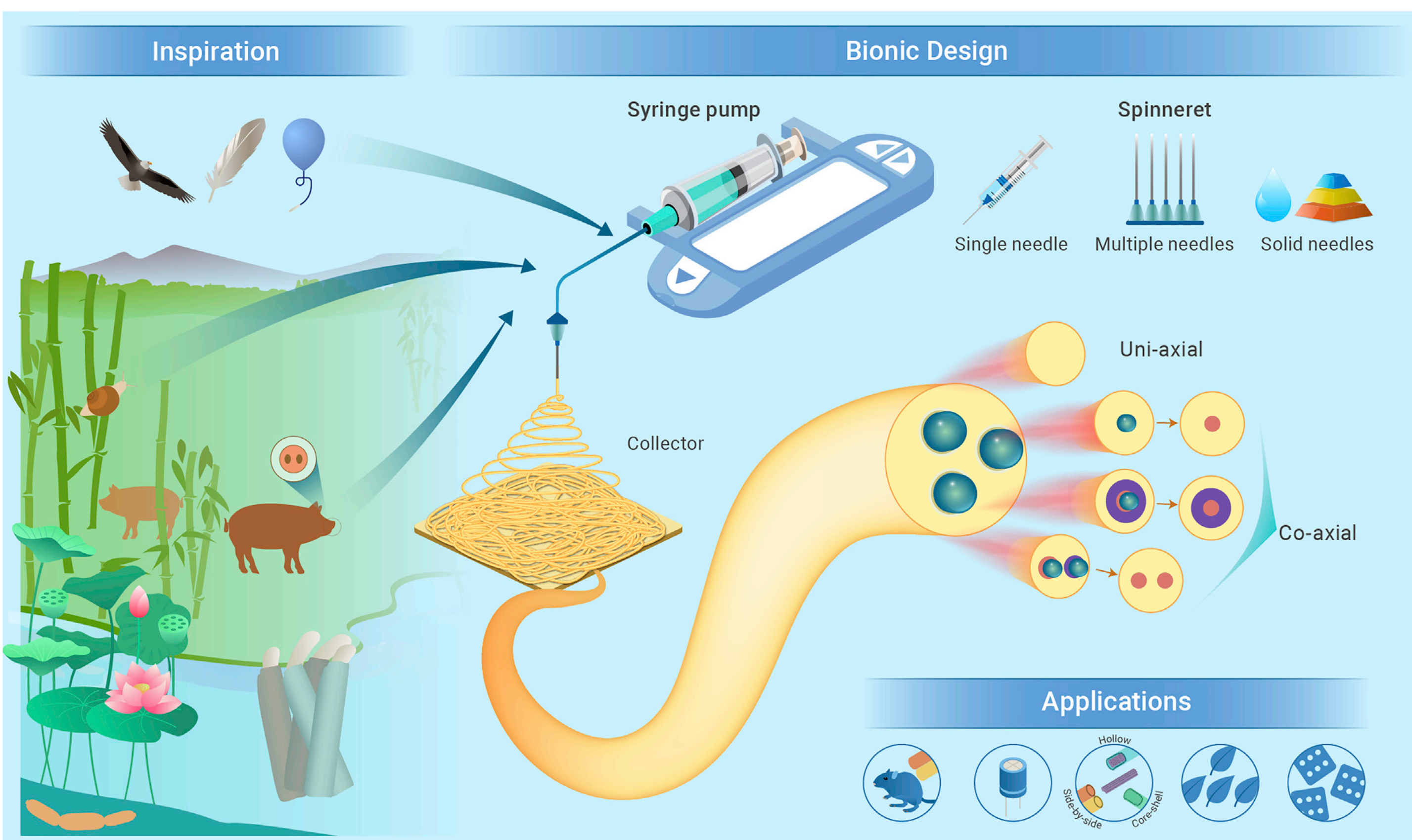

Figure 1. Bionic design of the electrospinning spinneret

of an animal or a plant in the design of an electrospinning spinneret may achieve unintended possibilities. The bionic design of the electrospinning spinneret can be observed in the electrospinning systems (Figure 1).

Traditional uniaxial electrospinning with a hollow spinneret uses a syringe and a needle, whereas the original design of the syringe and needle is assumed to have been inspired by animal bladders and goose feathers, respectively. With the development of electrospinning technology, the use of a coaxial needle renders electrospinning a powerful fabricating method, enabling the creation of nanofibers from materials that are not spinnable or that have a core sheath, as well as other types of structures.[2] Various templates that can be mimicked are available in nature. From studying the cross-section of hollow bamboo, a spinneret consisting of two coaxial capillaries with different diameters can be developed. During electrospinning with heavy mineral oil as the inner core and PVP/Ti(O*i*Pr)$_4$ as the outer shell, hollow TiO_2 tubular fibers can be obtained. Using this approach, a core-shell nanofiber or tubular fiber is prepared; however, creating artificial versions of multichannel tubular natural formations at the micrometer to nanometer scale remains a challenge. Mimicking the shape of razor clams renders the realization of nanowire-in-tube morphology feasible. With the design of three coaxial stainless-steel capillaries with different inner diameters, the inner, middle, and outer fluids can be separately fed. This design allows the separation of the outer and inner fluids of the TiO_2 precursor ($Ti(OBu)_4$ sol and ethanol solution) owing to the presence of the middle fluid of the liquid spacer layer (paraffin oil/water emulsion). In this process, the conductive exterior fluids can be stretched by an electrostatic force owing to charge repulsion when a high voltage is applied to the entire spinneret, and the middle and inner fluids are also collectively lengthened by the shear pressure. After calcination to remove organics, the TiO_2 nanowires are obtained in the TiO_2 tube. Therefore, inorganic structures can be successfully fabricated, and organic polymer composites composed of a polyacrylonitrile inner wire with an outer polystyrene shell can also be successfully generated.

The shape of a pig snout would have been an unlikely inspiration for a spinneret design.[3] Chang et al. used this bionic design, an oval-shaped tube with two channels, to generate the sheath stainless-steel capillary containing two inner stainless-steel capillaries in the center. The design of this unique spinneret for implementing trifluid electrospinning facilitated the fabrication of the sheath-separate-core nanofibers. Using this unique spinneret, three Eudragit copolymers could be developed with varied pH-dependent solubility in one sheath-separate-core nanofiber.

Lotus roots contain many channels and can be mimicked to fabricate multichannel tubular morphologies. Based on the cross-section of the lotus root, spinnerets with multifluid compound jet electrospinning can be developed. Specifically, for a three-channel tube spinneret, three metallic capillaries at the vertices of an equilateral triangle can be inserted into a plastic syringe. The fabrication of multichannel tubes with variable diameters and channel numbers, such as two, four, or five channels, is feasible in this manner.

The study of shellfish began more than 2,000 years ago with the Greek philosopher Aristotle. Later, the world discovered a beautiful pyramid-shaped fossil conch, the *Entemnotrochus rumphii*. An electrospinning spinneret with a similar solid pyramid-like morphology was designed, and finer nanofibers with narrow distribution were observed from this spinneret. More importantly, these bionic needle-less electrospinning setups have a high productivity of ∼4.00 g/h, which is much higher than the conventional single-needle productivity of 0.01–0.10 g/h.

The lotus seedpod provides a novel idea for the design of multineedle electrospinning. These hollow needles could be arranged not only into a linear array but also with certain geometric patterns, such as a circular, triangular, square, or hexagonal pattern. However, the paths of the jets often become irregular because of the electric field force and the coulombic force, and therefore the capability of this method is limited.

Bionic fiber design for advanced applications

The bionic design of the electrospinning spinneret provides a new possibility to fabricate unconventional fibers with various morphologies such as single hollow; sheath-separate-core; hollow fiber with two, three, four, and even more channels; and nanowire in microtube. The unconventional properties of fibers prepared by this novel technique offer a wide range of application potentials and pathways.[4,5] Several interesting examples and applications are listed as follows: (1) closed cavities in solid fibers are typically detrimental to the transfer and transport of substances; however, with hollow fibers, multiple chambers could easily be used for pollutant absorption, catalysis, supercapacitors, and batteries. (2) Multiple chambers within one fiber offer multidrug and functional combinability, with both therapeutics and diagnostics components integrated into one material. (3) Core-shell structures could provide a multilevel filtration effect, and the enlarged surface area could provide a large contact area with the target pollutant and electrolyte, for environmental and energy applications. (4) Electrospinning setups with special multiple-needle or needle-less solid spinnerets could provide high productivity for mixed nanofibers and possibly finer morphological control.

Although a subtle electrospinning spinneret design plays a key role in the final formation of fiber materials, several limitations exist. For example, the miscibility and compatibility of solvent must be carefully considered in coaxial electrospinning. Furthermore, a more detailed study of the relationship between the spinnerets and their fiber morphologies is required. Furthermore, bionic designed spinnerets have low productivity. As a future prospect, this innovative design is worth exploring further, with needle and needle-less electrospinning based on emerging and evolving bionic design. For needle electrospinning, recent advances in coaxial spinnerets could be used to fabricate hollow, core-shell, and more complex nanofibers by feeding different precursor solutions into the coaxial capillaries. Multineedle spinnerets offer the advantage of producing mixed nanofibers with high productivity. Significantly, needle-less electrospinning could offer a more unique bionic design for spinnerets without clogging issues. Therefore, these types of nanofiber jets could be operated simultaneously to increase the throughput. Studying spinneret designs based on natural objects has been an effective design method for preparing advanced fiber materials that meet real-world demands, and this approach will play an important role in future electrospinning technology.

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DECLARATION OF INTERESTS

The authors declare no competing interests.