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COMMENTARY

When bottom-up meets top-down

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Top-Down Man-Made Vs. Bottom-Up Nature

In nature, materials are built in a "bottom-up" manner, relying on the self-assembly of fundamental building blocks, and have evolved over thousands of years of natural selection to achieve impressive performance. Materials in nature are sustainably designed in a hierarchical and multifunctional way to be lightweight while also providing toughness and resilience, and to possess biotic and abiotic resistance. Since the industrial revolution and accompanying advancement of modern material science, most of our industrial materials are synthetic polymers and metals, which, unlike natural materials, are processed into products using a "top-down" approach. Many synthetic polymers are nondegradable, and their production processes are associated with a significant negative environmental impact. Marelli et al. (1) were the first to apply the top-down approach usually reserved for man-made materials to natural silk embedded with functional materials such as enzymes and light- and strain-responsive nanoparticles. This work was mainly possible due to the thermoplastic properties of silk, which enable compression molding, and its stiffness, which enables machining.

Silk and Its Applications

Significant attention has been accorded in recent years to biopolymers, mainly those with β-sheet–forming ability, such as silk, elastin, and fibrin. Silk fibroin is one of several structural proteins that can be used to generate biopolymer-based materials with controlled functionalities (2). The bottom-up process in silk fibroins is characterized by the formation of a hierarchical structure composed of β-sheets, which leads to superior stability and mechanical strength due to the higher molecular order (3). Silk self-assembly and crystallization can be controlled by a sol-gel-solid transition regulated through water evaporation (1, 4).

Silk has been used by mankind for hundreds of years in textiles and as surgical sutures. Today, regenerated silk fibroin can be transformed into a variety of unique formats, including films, fibers, nets, meshes, membranes, yarns, sponges, and hydrogels, in a water-based process that can be adapted to control degradation and include growth factors, drugs, and antibiotics for delivery applications. Compared with synthetic polymers that often elicit immune reactions and are toxic (5), silk fibroin does not induce a significant inflammatory response when implanted, thus enabling its use in medical devices for tissue engineering and regenerative medicine (6).

In addition to its biomedical use, silk fibroin has emerged as a highly promising biomaterial for biophotonic and electronic applications. Regenerated silk has been used in optical elements and photonic devices, such as optical waveguides, microlenses, sensors, imaging, and inverse opals (7–9). There are various strategies used in the fabrication of silk fibroin photonic and optical devices, including the spin coating, soft lithography, inkjet printing, and contact printing, and so on, of silk solutions (10). Another approach used silk-based photonic crystals in "eco-dyeing" to produce nature-based bistructural colors and inverse opals with structural colors spanning the UV visible–IR spectrum. Moreover, it was demonstrated that the colors of the silk-based photonic crystals could be controlled and tuned by humidity. The properties of regenerated silk inks can also be modified by combination with nanoparticles, such as ZnSe and CdTe quantum dots (9), to achieve white-light emission, or with azo-benzene side groups for optically induced birefringence and holography (11).

Most of the optical applications of silk have been demonstrated in films, which are ideal for optical devices because they are mechanically robust, have very smooth surfaces, are highly transparent and can be patterned with transverse features on the order of a few tens of nanometers. The direct printing of regenerated silk for use as optical waveguides has been reported and offers the opportunity to create biophotonic elements that are both biocompatible and biodegradable and can be readily doped or functionalized with a number of biologically active molecules (12). The optical properties of these waveguides further establish the efficacy of silk fibroin as a high-quality biocompatible optical material (8).

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See companion article on page 451.

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Silk inks are prepared in a water-based process that can potentially include a wide range of additives to further functionalize the ink, such as antibodies, lipids, growth factors, and functional polymers. The printing of functional biopolymeric inks allows for the customizable design of sensors and assays; for example, a printed colorimetric bacteria sensor was directly printed onto different matrices. Other examples of silk-based "bio-inks" include the combination of silk and HRP, which has the ability to preserve enzymatic activity, and silk with gold nanoparticles. The silk–gold ink was used for color engineering and surface plasmonic applications, where, when a green laser light was directed onto a paper printed with the ink, a topographical thermal distribution pattern was revealed on the printed pattern (13).

A Turning Point? Top-Down Nature

In their article, Marelli et al. (1) push the boundaries of the applications of silk materials into new fields that were traditionally dominated by synthetic polymers and metals. Fabrication methods such as compression molding and machining are typically used to produce large and complex objects such as car parts, engines, and plane parts as well as many commodity products, such as plastic eating utensils and packaging. The authors demonstrate that the silk fibroin sol-gel-solid transition was amenable to a top-down approach to create complex structures by evaporation of water to give cylindrical specimens that were then machined and polished into various shapes and surface microstructures and imprinted by compression molding at relatively low temperatures. Furthermore, the design of function for versatile applications was demonstrated by embedding functional elements into the precursor silk solution, for instance gold nanorods to produce a material that generates heat when exposed to a specific wavelength, or polydiacetylene vesicle pins that undergo a blue-to-red chromatic transition at the mechanical yield point.

Above all, the attractiveness of silk materials is based on their natural source, superior mechanical properties, ease of processing in water at conditions of ambient temperature and pressure, their compatibility with a wide range of additives for added material functionality, and their ability to be molded into a variety of forms using either a top-down or bottom-up approach. By combining bottom-up and top-down approaches, Marelli et al. (1) expand the applications of silk and also potentially of other biomaterials beyond the usual fibers, membranes, foams, and other soft materials. This study may indeed represent a turning point where two separate worlds meet to create new machines, engines, and structures that combine nature's nanometric, bottom-up self-assembling building blocks with man-made, top-down fabrication methods, such as molding, machining, and 3D printing, to produce not only better cars, airplanes, and packaging products, but also to give us the opportunity to impart life to today's still-lifeless objects.

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