CHAPTER

BIONIC SUPERFIBERS 17

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CHAPTER OUTLINE

1 INTRODUCTION

The natural presence of biominerals in the protein matrix and hard tissues of insects [1], worms [2], and snails [3] enables high strength and hardness (>500 MPa) of materials. Thus, the artificial incorporation of various nanomaterials in biological protein structures to obtain improved mechanical properties should, in principle, be possible. Silkworm cocoon is a by-product of a natural process to protect butterflies from environment and predators and can be considered as a natural polymer composite consisting of continuous fibers with a length of about 1000 m and diameters of 10–30 μm, which are glued together by sericin [4–6]. Feeding *Bombyx mori* silkworms with diets containing carbon nanomaterials could result in intrinsically reinforced silkworm silk fibers. For example, it is known that acetobacter bacteria spin cellulose—as a by-product—as it consumes glucose, the reasons for which are unclear, but it is thought the material might protect the bacterial colony from external contamination. Therefore, fermentation of bacteria in the presence of nanomaterials could create a biogenic composite. Starting with a small jar, it is possible to transfer large cultures until to obtain material enough to create composites with unexpected properties. This approach offers new possibilities to biogenic reinforced composite manufacturing. Yeast is a cellular factory and reproduces asexually through a process called "budding" in which a "mother" cell grows a "daughter" cell that separates to become fully

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independent. Yeast fermentation could be exploited to transfer carbon nanomaterials from one yeast cell to another by internalization process or to replicate 2D materials on the cell walls [7, 8]. These techniques used commercially available bread yeast but can be generalized to any living cells without special surface modification of nanostructured carbon materials. In turn, this process could lead to the development of hierarchical and interactive structures programmed to self-assemble into specific patterns, such as those on strain sensors, and of self-healing materials capable to sense and repair mechanical damage. In this context, these studies could have future implications of biomaterials in the manufacture of bionic superfibers with improved mechanical properties and a toughness modulus surpassing synthetic polymeric high-performance fibers [9] and even the current toughest "knotted" fibers [10–12].

2 BIONIC SILK

Animal-produced silks (especially not only spiders but also silkworms and others) are recognized for their outstanding mechanical properties, and experimental attempts have been made to emulate the properties of natural silk by means of the production of regenerated silk fibers [13–15]. Natural silk fiber is a hierarchical material where hydrogen-bonded β-strands, β-sheet nanocrystals, and a heteronanocomposite of stiff nanocrystals embedded in a softer semiamorphous phase assemble into macroscopic silk fibers. It follows that the large breaking stress of silkworm silk fibers can be explained according to the hierarchical structures of the crystal domain and network [16]. In view of their surprising strength, the utilization of silkworm silk fibers as reinforcement for polymer composites is gaining attention in different fields of applications. Several attempts have been done in this regard: Hu et al. [17], for example, were able to regulate the crystallinity of regenerated silk fibroin by exposing silk to hot water vapor; Zhang et al. [18] showed the preparation of silk directly dissolving fibers in $CaCl_2$-formic acid, preserving nanofibril structure and allowing high-quality silk materials, while recently, Buehler et al. [19] reported a bioinspired spinning method to obtain regenerated silk fibers, by pulling silk microfibril solution. However, these methods exploit dissolution and posttreatment processes that are time-consuming and require solvents that are difficult to remove and in some cases are toxic, and in general, the achievement of the natural β-sheet crystal structure is challenging [20–22]. Carbon nanotubes (CNTs), which possess superior mechanical properties, are widely applied as reinforcement in preparing high-performance materials [23–26]. A number of groups introduced such nanoparticles with a nonbionic approach [27] on the surface of spider silk fibers, achieving an enhancement of toughness [28] or electric conductivity [27]. Recently, the in vivo incorporation of CNTs into spider silks has been explored (Fig. 1) [29].

In Fig. 2, the strength and toughness of various natural and artificial materials are compared. The silk/CNT fiber obtained in the study of Pugno et al. [29] displayed a strength higher than synthetic polymer fibers like Zylon or Endumax or CNT-/carbon-reinforced polymeric fibers [30–32]; at the same time, the toughness of bionic silk/CNT fiber is higher than the toughest spider silks found in nature [33].

Along with spider silk that remains challenging to produce on industrial scale, silkworm silk fibers are available on large scale and have been integrated in bioengineering structures in which they serve as a model of lightweight composites [34–39]; in fact, after removing the sericin, silkworm silk could be used as natural fiber in the composite industry replacing glass and carbon fibers [40]. Feeding *B. mori*

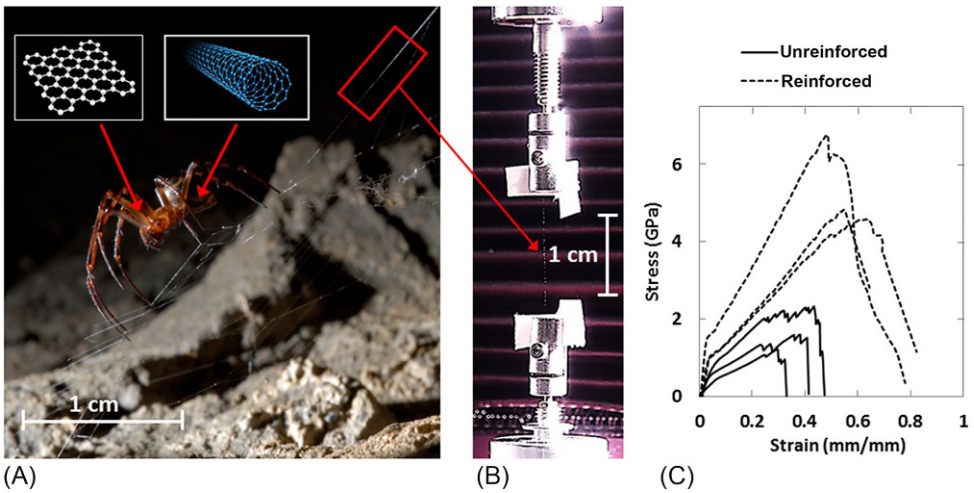

FIG. 1

Schematic of the experimental procedure. (A) Spiders are fed with dispersions containing graphene or CNTs; (B) the corresponding spun silk is collected and tested in a nanotensile system; (C) stress-strain curves show improved mechanical properties when compared with pristine samples [29].

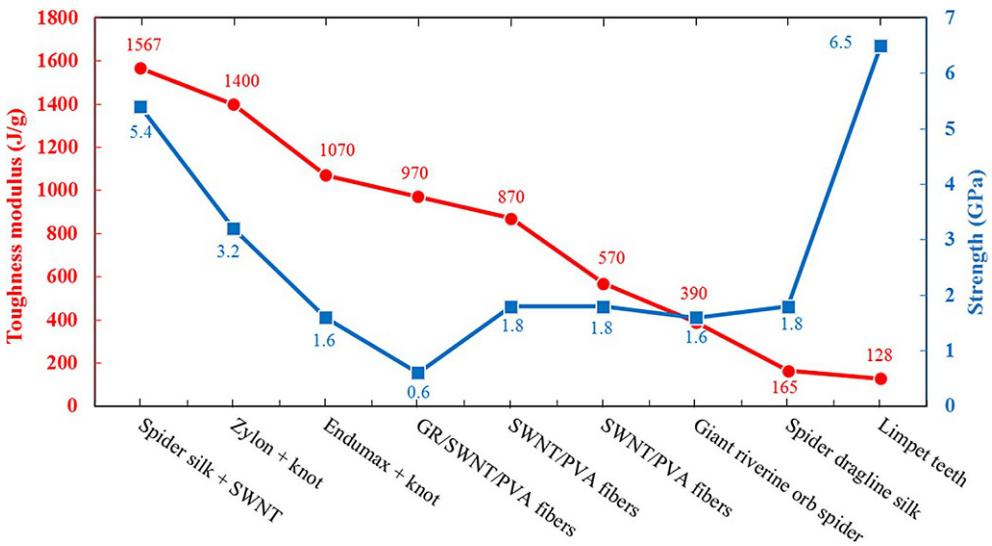

FIG. 2

Toughness modulus and strength of different materials and composites [29].

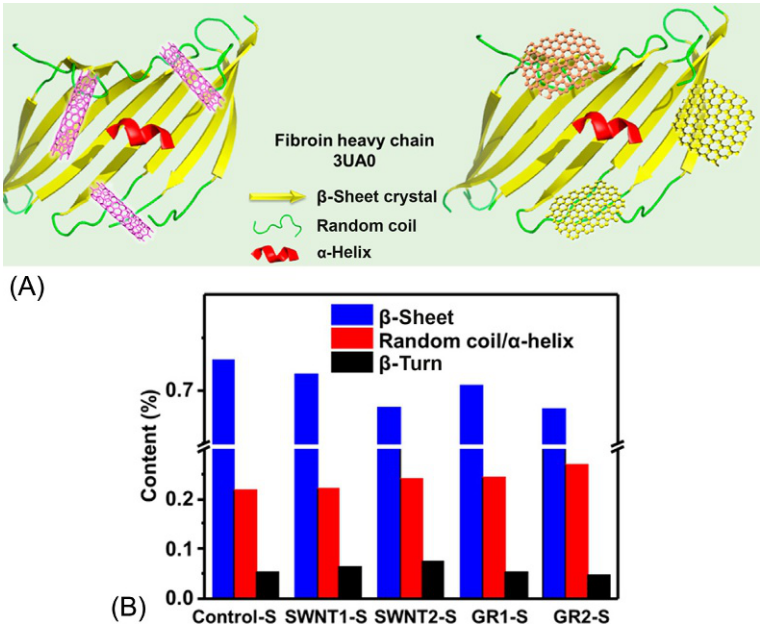

FIG. 3

Influence of CNTs on the crystalline structure of silkworm silk fibers. (A) Schematic illustration showing the interactions between CNTs and silk and (B) content of secondary structures in different silk samples [41].

silkworms with diets containing CNTs led to intrinsically reinforced silkworm silk fibers [41]. The silk fibers produced by such natural process showed superior tensile strength and toughness thanks to a spontaneous silk spinning process that converts helical and random coils to β-sheet structures; because the mechanical properties of silk fibers are highly related to the secondary structure, which consists of helical and random coils, β-sheet, and β-turn (see Fig. 3), the toughness of such bionic silk fibers was tuned through adjusting the proportion of the secondary structure of silks revealing that the CNT-modified silks contained more α-helix and random coil structures (Fig. 3).

3 BIONIC YEAST

Yeast is a cellular factory that is capable of taking simple molecules from its environment, such as sugars, and synthesizes new elements needed for its growth at mild temperature [42–45], and thus, empty yeast cell represents an ideal case study for nanomaterial encapsulation. Water is an important factor; in this regard, dry yeasts become fully impermeable to molecules, whereas wet yeasts promote the transfer of molecules from outside to inside the cell. Many biological processes taking place inside the living cell rely on the nanomechanical properties of the cell wall, and the synthetic combination of inorganic functional materials with cells further enhances their functionality and application in devices and sensors [46, 47]. Considering the conducting nature of CNTs, the interactions between

microorganism and carbon nanotubes could be used for generating bionic nanomaterials with unexpected mechanical and electric properties. Such living materials can be considered as bionic materials because they have the benefits both of biological world that can self-organize and of nonliving materials that add functions such as strength and electronic transport [7, 48].

The mechanism of nutrition and growth of microorganism represents an unexplored field to design interface between microorganism and such nanomaterials. Valentini et al. [7] adopted a strategy based on *Saccharomyces cerevisiae* yeast cells that multiply with a process where a daughter cell is initiated as growth from the mother cell. They exploited such mechanism to obtain the intracellular transport of CNTs during this growth process (Fig. 4); the strength of the composite was also estimated from the pullout energy at the CNT-yeast interface (Fig. 5).

Another important class of bionic materials takes inspiration from the method that the microorganisms use to assemble in fast way hybrid porous nanostructures. Thus, microorganisms can facilitate the formation of a wide range of porous nanomaterials that have unique physical properties and structures that are not produced by abiotic processes. More recently, the metabolic activities of biological processes such as beer fermentation were adopted to generate porous hierarchical composites in gelling materials during their cross-linking or auxetic bionic porous nanocomposites [49, 50]. High porous bionic hybrid materials made of cardiac cells and CNTs might also provide muscle for robots made of living tissues [51]. Khademhosseini et al. [51] realized a hybrid scaffold, with CNTs homogeneously incorporated into a gelatin derivative, and addressed simultaneously the three principal requirements

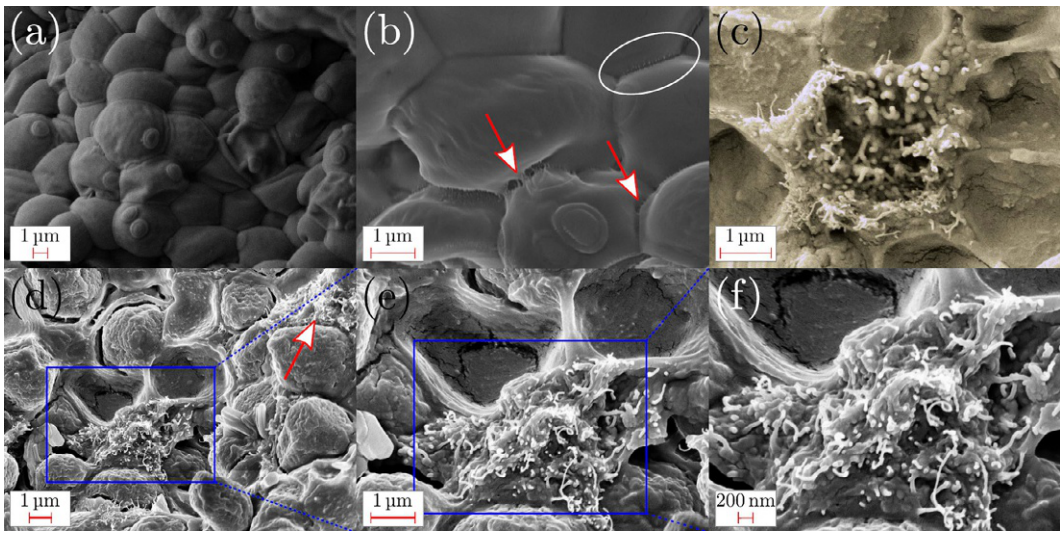

FIG. 4

(A) Field emission scanning electron microscopy (FESEM) image of *Saccharomyces cerevisiae*. (B) FESEM image showing CNTs bridging yeast cells. The *arrows* indicate the CNTs bridging the yeast cells. (C) FESEM image of the cross section of the fermented yeast/CNT film after prolonged exposure to FESEM where CNTs protruding from a broken yeast cell are visible. (D–F) FESEM images of the yeast/CNT film without fermentation taken at different magnifications [7].

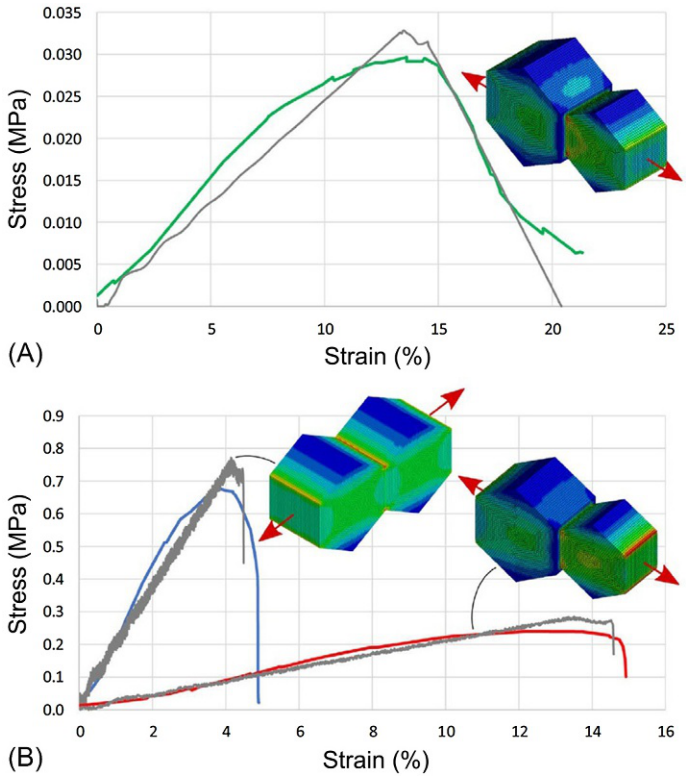

FIG. 5

Stress-strain curves obtained from tensile tests on (A) fermented yeast sample (*green curve*) and (B) yeast/CNT composites prepared before fermentation (*blue curve*) and after fermentation (*red curve*), respectively. Note that for the fermented system, two different cell types in terms of dimension and mechanical properties were adopted in order to take into account the mother-daughter cell systems. The comparisons with the result of finite element method (FEM) simulation of traction of a two-cell system are also reported [7].

for tissue engineering: high porosity for cell adhesion, biodegradability, and high elastic tensile/compressive modulus. Due to the fiber-like structure, high electric conductivity, and high mechanical strength of CNTs, the porous gelatin framework was strengthened with a reduced electric impedance. The fractal-like CNT networks were found also to alter tissue organization (Fig. 6), which are particularly suitable as cell delivery system for cell therapy.

4 BIONIC CELLULOSE

Composites consist of a material with a high strength, reinforced with a ductile and tough phase, and are very important in advanced material design [52]; there exist examples in attaining both strength and toughness, which often involve complicated geometries (e.g., carbon nanotubes connected by

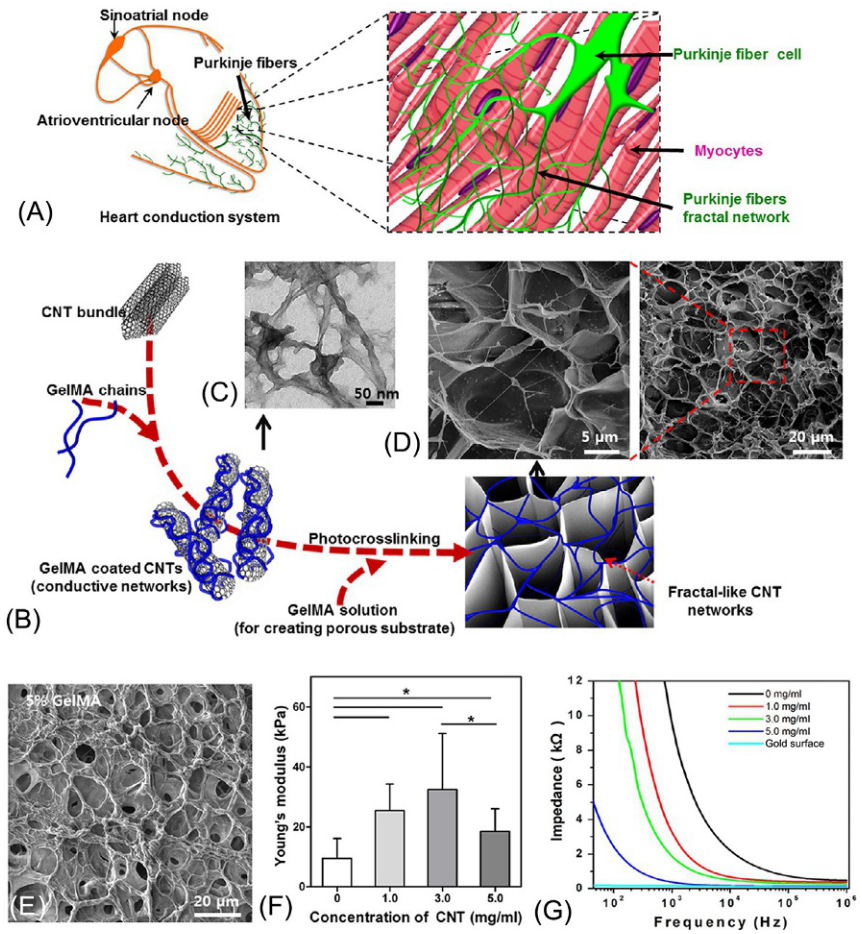

FIG. 6

Structural, physical, and electric characteristics of CNT-photo-cross-linkable gelatin methacrylate (GelMA) hydrogels [51]. (A) Schematic diagram illustrating the isolated heart conduction systems showing the Purkinje fibers, which are located in the inner ventricular walls of the heart. (B) Preparation procedure of fractal-likeCNT networks embedded in hydrogel. (C) TEM image of hydrogel-coated CNTs. (D) SEM images show porous surfaces of CNT-hydrogel thin film. (E) SEM images of pristine hydrogel. (F) Young's moduli of CNT-hydrogels. (G) Decreasing of the overall impedance of a 50 μm thick hydrogel thin film with increased CNT concentrations.

Y-junctions forming a supergraphene) [53] that are hardly applicable to other materials. A general approach to address the conflict between strength and toughness still remains challenging. Recently, Zhu et al. have reported a study on the mechanical properties of cellulose-fiber-based paper [54], where they observed that both the strength and toughness of cellulose nanopaper increase simultaneously (40 and 130 times, respectively) as the size of the constituent cellulose fibers decreases (from a mean diameter of 27 μm to 11 nm), revealing an anomalous but highly desirable scaling law of the mechanical properties of cellulose nanopaper: the smaller, the stronger and the tougher (Fig. 7).

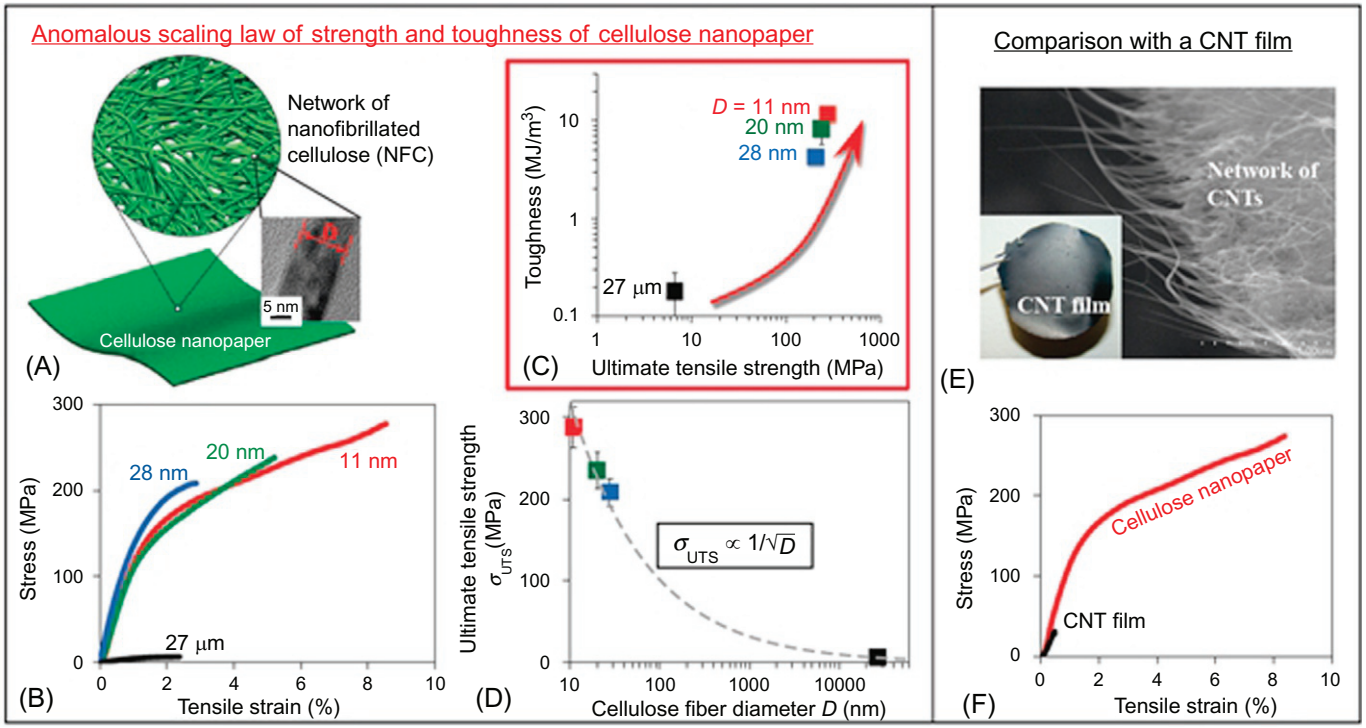

FIG. 7

An anomalous scaling law of strength and toughness of cellulose nanopaper: the smaller, the stronger and the tougher [54]. (A) Schematic of cellulose nanopaper, made of a random network of CNF fibers. (Inset) High-resolution transmission electron microscopy (HRTEM) image of an ~11-nm CNF fiber. (B) Stress-strain curves of cellulose paper made of cellulose fibers of various mean diameters. As the cellulose fiber diameter decreases from micrometer scale to nanometer scale, both tensile strength and ductility of the cellulose paper increases significantly, leading to an anomalous scaling law (C): the smaller, the stronger and the tougher. (D) Reveals that the ultimate tensile strength scales inversely with the square root of cellulose fiber diameter. (E) SEM image of a carbon nanotube network and (F) comparison with tensile properties of cellulose nanopaper.

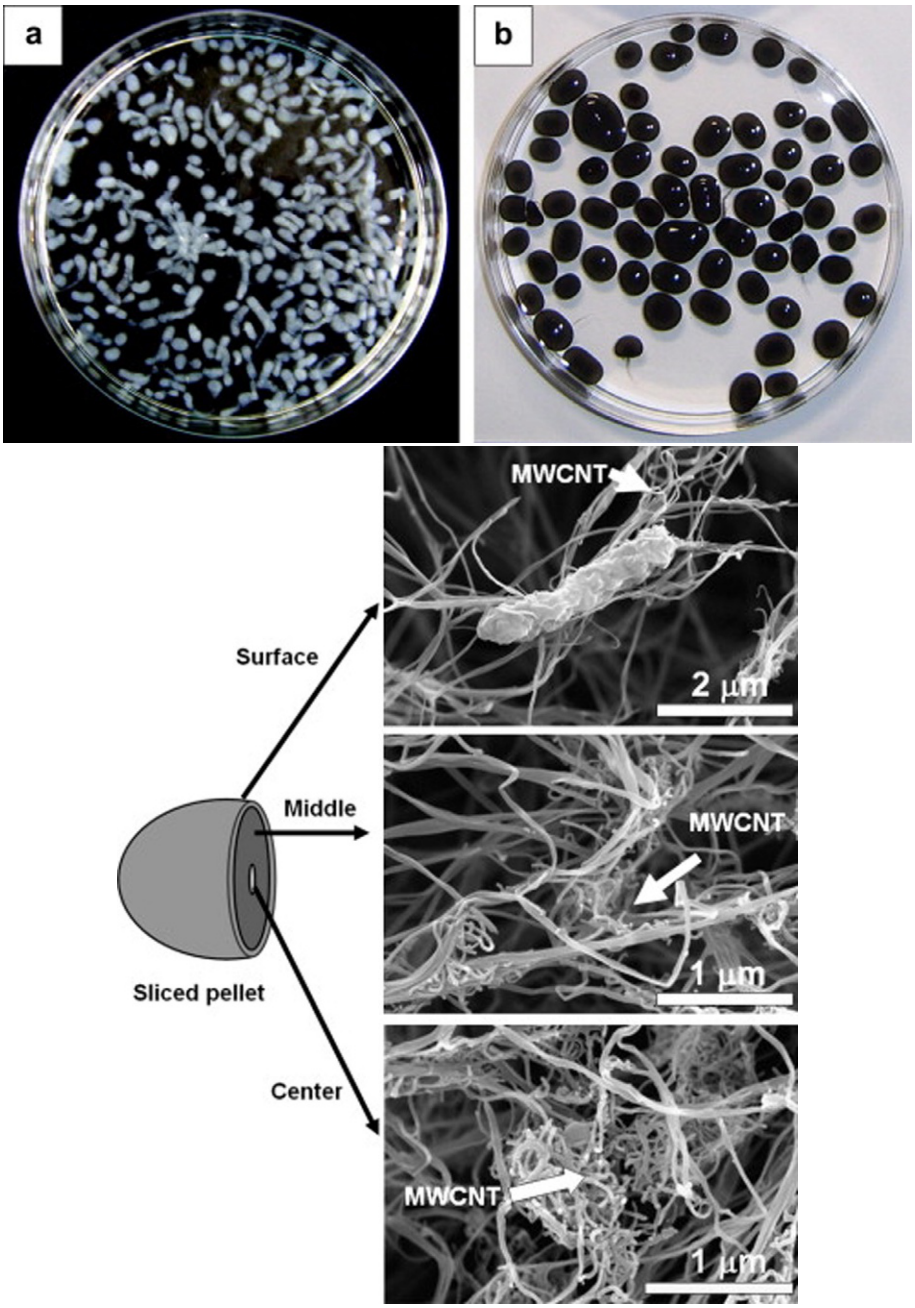

FIG. 8

Photographs of bacterial cellulose pellets synthesized in (A) Hestrin and Schramm medium and (B) multiwalled carbon nanotube (MWCNT)-dispersed Hestrin and Schramm. (C) FESEM images of bacterial cellulose synthesized in MWCNT-dispersed Hestrin and Schramm medium [57].

Many different types of cellulose can be found in plants or microorganisms. Among these, bacterial cellulose (BC) harvests a specific interest in the field of biogenic materials because it is a specific product of the primary metabolism of bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina* [55]. Because of its unique properties resulting from the ultrafine structure, BC can be transformed into regenerated materials (fibers, films, food casings, membranes, sponges, etc.) [56]. Extracellular polymeric secretions (EPS) of such bacteria are multipurpose polymers that are important for applications in several fields. The preparation of bionic fibers of BC when EPS are involved in bacterial nutrition or interaction of bacteria with CNTs was reported by Park et al. (Fig. 8) [57].

The mechanical properties of such bionic fibers were also investigated [58], and the results are reported in Fig. 9 where Young's modulus of the pristine BC, BC fiber, and BC/CNT fibers was 7.3, 29.2, and 38.9 GPa, respectively. Young's modulus of the bionic composite fibers was approximately 430% higher than that of the pristine BC. The major finding of this study lies in that the well-aligned hybrid microfibers are much stronger and tougher than the microfibers composed of nanofibrillated cellulose or CNT alone.

Further, molecular dynamics simulations [59] revealed that the synergetic interaction of hydrogen bonds between the nanocarbons and cellulose nanofibrils is the key to the enhanced mechanical performance (Fig. 9). The variation of total hydrogen bonding energy, which matches well with that of the total potential energy in terms of both peak location and amplitude, offers strong evidence for the cascade of events of hydrogen bond breaking and reforming during the sliding process and the dominant role of hydrogen bonding in the toughening mechanism of cellulose nanopaper. The magnitude of

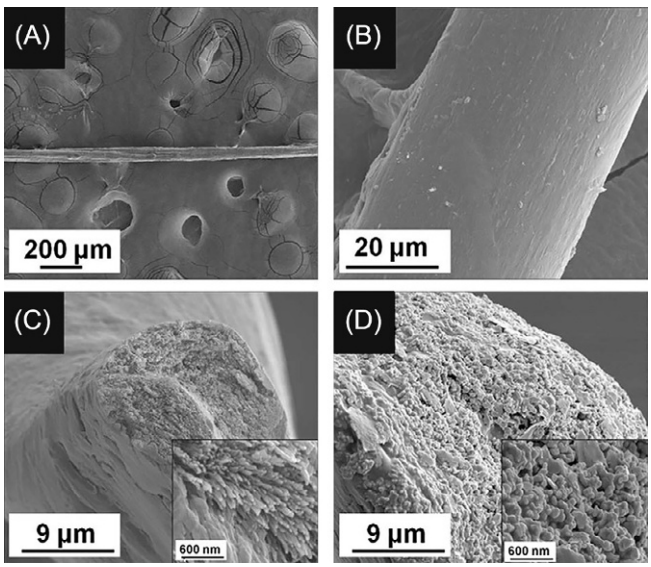

FIG. 9

SEM images of the regenerated BC/MWCNTs composite fibers (A) and (B), and the cross-sectional fracture and the enlarged cross-sectional fracture of a regenerated BC fiber (C) and regenerated BC/MWCNTs composite fiber (D) [58].

resistant force in cellulose fiber case is substantially higher than that in the CNT case, shedding light on molecular-scale understanding of the huge difference in tensile strength between cellulose nanopaper and CNT films. The synergistic interaction between cellulose fibrils and CNT is thus applicable to other material building blocks facilitating a new design strategy to create a wide range of mechanically strong bionic microfibers.

5 CONCLUSION

The new emerging field of bionics (according to our strict definition) could lead to a revolution in materials science thanks to the production of superior materials directly by evolved organisms (such as spiders or silkworms) when in the presence of artificial nanomaterials (such as graphene or CNTs). In this sense, bionics is the natural evolution of biomimetics.

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