Biomimetic twisted plywood structural materials

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ABSTRACT

Biomimetic designs based on micro/nanoscale manipulation and scalable fabrication are expected to develop new-style strong, tough structural materials. Although mimicking nacre-like “brick-and-mortar” structure is well-studied, many highly ordered
natural architectures comprising one-dimensional micro/nanoscale building blocks are still elusive to be imitated owing to the scarcity of efficient manipulation techniques for micro/nanostructural control in practical bulk counterparts. Herein, inspired by natural twisted plywood structures with fascinating damage tolerance, biomimetic bulk materials that highly resemble natural hierarchical structures and toughening mechanisms are successfully fabricated through a programmed and scalable bottom-up assembly strategy. By accurately engineering the arrangement of one-dimensional mineral micro/nanofibers in biopolymer matrix at multiscale, the resultant composites display optimal mechanical performances, superior to many natural, biomimetic and engineering materials. The design strategy allows for precise micro/nanostructural control at macroscopic three-dimensional level and can be easily extended to other materials systems, opening up an avenue for many more micro/nanofiber-based biomimetic designs.

**Keywords:** biomimetic designs, micro/nanoscale building blocks, twisted plywood structures, damage tolerance, biomimetic bulk materials, toughening mechanisms

**INTRODUCTION**

Biological materials, though composed of relatively sterile components (brittle calcium- or silicon-based minerals and ductile biopolymers), possess intriguing mechanical performances owing to their precise hierarchical structures over several length scales originating from nanoscale building blocks [1-3]. They are increasingly becoming the model materials for scientists and engineers to mimic and then design new-style strong and tough structural materials. Besides the extensively studied “brick-and-mortar” structure in nacre comprising two-dimensional (2D) building blocks and a small amount of biopolymers [1,2], more exquisite hierarchical structures based on highly ordered arrangement of one-dimensional (1D) micro/nanoscale building blocks are also evolved in many biological materials and impart their excellent mechanical performances [2-5]. Especially, twisted plywood (Bouligand-type) structures in *Arapaima gigas* scale, lobster claw and lamellar bone endow them with exceptional damage resistance [3-7] that is highly desirable for structural engineering materials to improve their
durability and reduce the risks of catastrophic damages.

Over the past decades, great achievements have been made in bioinspired structural design [8-11], especially for nacre-mimicking fields [12-19]. However, designing high-performance macroscopic materials by imitating 1D micro/nanofiber-based hierarchical structures (such as twisted plywood structures) of natural biological materials has rarely been exploited. In contrast to in-plane isotropic 2D building blocks, 1D micro/nanoscale building blocks are more flexible for spatial arrangement [20]. Though some assembly techniques, such as Langmuir-Blodgett (LB) [21], nanocombing [22], strain-release [23] and knocking-down [24] have been well-developed for aligning 1D micro/nanoscale building blocks on 2D substrates, it remains infeasible to organize them into hierarchically ordered structure at macroscopic three-dimensional (3D) level due to the inevitable technical limitations. Therefore, for most fiber-reinforced composites, the individual and finite long 1D micro/nanofibers (reinforcements) are just randomly distributed in the matrixes, leading to the limited mechanical enhancement [25,26]. Recently, electrically assisted 3D printing technique demonstrated the possibility in aligning 1D nanofibers and constructing biomimetic anisotropic reinforcement architectures, but relatively limited materials choices and complicated operational processes may be two restrictions for its effective extension [27]. Thus, it is quite desirable to exploit a facile, versatile and scalable strategy for orderly integrating 1D micro/nanoscale building blocks into macroscopic 3D hierarchical architectures (such as twisted plywood structures) resorting to natural inspirations.

By observing the micro/nanostructure of Arapaima gigas scales (Supplementary Fig. 1), we can find distinct twisted plywood structure which is formed by superimposing planar layers of parallel-aligned micro/nanofibers with a tiny angular deviation [4,5]. Inspired by this special two-level architecture, we proposed a universal, programmed and scalable bottom-up assembly strategy for fabricating macroscopic 3D artificial twisted plywood structures based on 1D micro/nanoscale building blocks. Brushing-induced assembly method was proposed to flexibly arrange 1D micro/nanofibers in polymer matrixes to first construct biomimetic inorganic-organic 2D films with predefined structures (unidirectional or twisted arrangement of micro/nanofibers), controlled periodicities and thicknesses, which were then facilely and efficiently laminated into macroscopic 3D bulks. The resultant bulk composites exhibit comprehensive mimicry of both hierarchical structures and
mechanical characteristics of their natural counterparts, demonstrating that high-performance artificial twisted plywood structural materials in practical bulk form can be readily obtained relying on this two-level assembly strategy due to its possibility for precise structural control from micro/nanoscale to macroscale.

RESULTS AND DISCUSSION

Brushing-induced assembly of 1D micro/nanofibers into macroscopic ordered 2D films

Hydroxyapatite (HA) mineral microfibers (Supplementary Fig. 2) and sodium alginate (SA, biopolymer) were adopted here as the typical inorganic 1D building blocks and polymer matrix, respectively, due to their biocompatibility and good interface interaction. In order to align HA microfibers in SA matrix and obtain large-area freestanding HA-SA films with predefined ordered structures, brushing-induced assembly strategy was developed here (Fig. 1a and Supplementary Fig. 3). In brief, commercially available brush adsorbed with HA-SA dispersion was sliding on a hot planar substrate along a certain direction, and 2D films containing ordered arrangement of HA microfibers embedded in SA matrix can be gained after solvent evaporation. The brush used in our experiments exhibits significant capacity for holding HA-SA dispersion, attributed to the special structural characteristics of brush hairs (conical shape with nonuniform distribution of squamae along its longitudinal axis) (Supplementary Fig. 3b) and Laplace pressure difference [28,29]. These two factors synergistically maintain HA-SA dispersion between quasi-parallel brush hairs. During this dynamic balance process, the characteristic length of HA microfibers is larger than the space of two adjacent brush hairs, while the diameter of HA microfibers is much smaller than that of the brush hairs, thus, the flow-shear stress and the characteristic length difference would be beneficial to the pre-alignment behavior of HA microfibers in the dispersion confined between adjacent brush hairs (Supplementary Fig. 3a and c). During the slightly brushing process, only finite-length brush hairs connected with the substrate and maintained quasi-parallel configuration, thus the HA-SA dispersion between every two adjacent brush hairs was transferred onto the substrate due to the large solution-substrate interaction (wettability). In the meantime, the possible Ca$^{2+}$-COO$^{-}$ coordination between HA and SA [13] and relatively high viscosity (measured to be 540 mPa·s) of SA solution provided the embedded HA
microfibers with larger interaction with the solution than that with the brush hairs. Therefore, the pre-aligned HA microfibers were transferred onto the substrate with long axis along the brushing direction during the brush stroking process (Supplementary Fig. 3d). In addition, the relatively viscous polymer solution could effectively limit free movement of these aligned microfibers. With further assist of heat-induced solvent evaporation, large-area composite films containing orderly arranged HA microfibers can be gained (Fig. 1b inset).

Scanning electron microscope (SEM) images and nanoscale computed tomography (Nano-CT) images demonstrate that HA microfibers are almost parallel to each other in the resultant films (Fig. 1b, c and Supplementary Fig. 4), which are distinct from those of disordered HA-SA film prepared by self-evaporation (Supplementary Fig. 5a and b). Birefringence effect [30] was further adopted to identify the large-scale structural orderliness of the resultant films. The ordered HA-SA film located with different azimuth angles (relative to the directions of orthogonal polarizer and polarization analyzer) displayed distinct birefringence characteristic (Fig. 1d) due to the intrinsic birefringence of HA single-crystal microfibers (Supplementary Fig. 6a) and the macroscopic structural orderliness. In contrast, disordered film did not show this characteristic because randomly dispersed HA microfibers in SA matrix invalidated the rotation operation (Supplementary Fig. 5c). X-ray diffraction patterns [3] also confirmed the orientation of HA microfibers in the ordered HA-SA film. The special (002) crystal face of HA microfibers appeared as a short circular arc for the ordered film, whereas it appeared as a nearly whole circle for the disordered film (Fig. 1e and Supplementary Figs 5d, 6b and c). In addition, mechanical anisotropy of the ordered film further reflected the structural orderliness (Supplementary Fig. 7). All these aforementioned structural and mechanical characterizations demonstrate the feasibility of brushing-induced assembly method for aligning 1D HA microfibers. Furthermore, as the HA microfiber aligned direction is parallel to the brushing direction at each brushing process, we can not only achieve large-area composite films with unidirectional arrangement of HA microfibers, but also fabricate films with helically arranged microfibers by programmed and continuous brushing with each brushing process twisting a predefined deviation angle (Fig. 1f and g).

Owing to the universality, flexibility and simplicity, this assembly method is also suitable for accurately aligning other 1D
micro/nanoscale building blocks and fabricating relevant composite films. It was found that several exemplifications of micro/nanofibers, including silver nanowires, calcium carbonate whiskers and xonotlite nanowires were all orderly arranged in polymer matrixes (Supplementary Fig. 8). Specifically, when applying the brushing procedures with predefined deviation angles to xonotlite nanowires dispersed in SA solution, biomimetic composite films with periodically ~90° cross-stacked structure and helically arranged structure can also be obtained (Fig. 1h and i).

**Fabricating macroscopic 3D biomimetic twisted plywood structural materials**

In fact, developing appropriate and scalable methods for preparing biomimetic structural materials in practical bulk form from micro/nanoscale building blocks is still a significant challenge [8,13]. Here, after achieving the first-level assembly, these obtained biomimetic 2D HA-SA films with predefined unidirectional or twisted arrangement of 1D micro/nanofibers were then used as second-level building blocks to readily replicate the unique natural micro/nanofiber-based twisted plywood structures into more practical 3D bulk materials via flexible laminating strategy (Fig. 2a). This two-level “brushing-and-laminating” assembly strategy is intrinsically a bottom-up technique for fabricating macroscopic bulks, which allows for multilevel structural control and exhibits great potential for scalable biomimetic preparation. As expected, SEM images show that the resultant materials exhibit distinct twisted microstructures (Supplementary Fig. 9). Furthermore, multitudinous slices (cross-sectional direction) of the prepared twisted plywood structural material visually reveal the periodically helical structure at larger scope (Supplementary Movie 1). Moreover, by extending the hierarchically structural control to thinner nanowires, macroscopic 3D biomimetic nanocomposite material with more elaborated twisted plywood structure was also realized (Supplementary Fig. 10). Overall, precisely manipulating the arrangement of 1D micro/nanofibers for designing macroscopic 3D biomimetic twisted plywood structures similar to those found in nature can be successfully achieved.
Mechanical analyses of biomimetic twisted plywood structural materials

To explore the contribution of the biomimetic structural designs to the ultimate mechanical performances, systematic mechanical tests were conducted. Same as the optimal 2D HA-SA films (Supplementary Fig. 11a), the 3D bulk material containing ~40 wt.% HA microfibers also exhibited the most desirable mechanical performances (Supplementary Fig. 11b). Flexural strength and modulus of these obtained materials gradually declined with increasing deviation angles (from 0° to 90°) (Fig. 2b). It is noteworthy that, the ~10° twisted specimen still maintained a high level of strength and modulus (257.7 MPa and 15.6 GPa) which were much higher than those of ~90° and ~45° twisted specimens. In principle, except for strength, high toughness is another primary target for structural materials to improve their durability and reduce the risks of catastrophic damages. In this work, the biomimetic 3D bulk materials with small angle twisted plywood structures (~10° and ~20° twisted specimens) exhibited excellent fracture toughness and distinct crack resistance curve (R-curve) behavior, which were superior to those of other specimens with larger angle twisted structures (Fig. 2c-h). In addition, the fracture toughness can be further improved by reducing the periodical thickness of twisted plywood structures (namely, reducing the thickness of each unidirectional fiber lamella) (Supplementary Figs 12 and 13) [7,31].

In typical natural twisted plywood models, cracks always extend along twisted propagation paths between adjacent fiber layers (Fig. 3a), because crack tips have more probabilities for circumventing rather than severing these strong 1D micro/nanofibers. Thus, during main directional crack extension, total energy dissipation will be enlarged due to the larger interfacial area per unit crack length, leading to the high damage tolerance [3,6,7,31]. To some extent, our designed small angle twisted plywood structural materials successfully replicate natural toughening mechanisms, underlying the excellent macroscopic mechanical characteristics. The captured SEM images reveal that crack propagation paths in the artificial materials are partly parallel to the axial direction of HA microfibers and deflect between adjacent HA-SA layers (Fig. 3b and Supplementary Fig. 14). It was observed that the main crack displayed complicated twisted state at larger scope, and many microcracks ahead of the crack tip could be found (Fig. 3c-e and Supplementary Movie 2). These phenomena are identified
as important toughening mechanisms for many structural materials [8,13,32,33]. In contrast, for the bulk material with unidirectionally aligned HA microfibers, relatively straight crack gradually emerged during single-edge notched bend (SENB) test when the bend direction was parallel to the longitudinal axis of HA microfibers (Fig. 3f), demonstrating obviously low damage tolerance (Figs. 2e, i and 3g). Finite element method (FEM) simulations were then performed to uncover the damage morphology inside the biomimetic twisted plywood structural materials. Two different failure modes demonstrate that the designed biomimetic structure results in a twisted fracture pattern (Fig. 3h-k). Due to the finite length of HA microfiber, experimentally observed macroscopic complicated crack pattern can be regarded as the main reflection of numerous simulated local twisted crack morphologies. These multiscale crack-related observations and FEM simulations (Fig. 3 and Supplementary Fig. 14) synergistically manifest that the crack tips are inclined to parallel to HA microfibers rather than directly severing them in the biomimetic twisted plywood structural materials, demonstrating great similarity to the micro/nanoscale-based toughening mechanisms found in natural materials.

To gain more insight into the deformation mechanisms of the designed biomimetic materials, molecular dynamics (MD) simulations of multilayer microfibers with twisted arrangement styles were performed. The mechanical performances of twisted plywood structural materials are related to those of single microfiber and the helical stacking behavior of the closely pitched microfiber lamellas. Therefore, coarse-grained MD simulation of elastic bead-spring model was adaptable to theoretically investigate the mechanical behavior [5]. Firstly, simulations of unidirectional microfiber lamellas under tension mode demonstrated that there were three different typical deformation modes, including delamination, shear deformation, and rotation (Fig. 4a-d and Supplementary Figs 15-17). It was found that the delamination and shear behavior were important mechanisms for releasing the deformation energy stored in microfibers, due to these formed microcracks along them (Supplementary Figs 16-18). Then, the tension behavior of these helicoidally stacked microfibers with successive layers, based on the model of microfiber lamellae with 20° layer deviation angle, was investigated, manifesting combined and coupled deformations (Fig. 4e-h and Supplementary Fig. 19). Global and local deformations and structural slices illustrated
that the delamination and bridging behavior of microfibers firstly appeared in the stretched model due to the large deviation angle of some layers. Although the microcracks and delamination had appeared, other layers with small deviation angles did not show obvious deformations. With further tension (larger strain), those layers with small deviation angles just displayed shear and rotation deformations. Based on MD simulations, we can infer that, during the loading process, the microfibers with small deviation angles are rotated along with the tensile direction to resist the tensile loading, while the microfibers with large deviation angles will dissipate more energy through shear deformation, delamination and gradual microcrack propagation (See Supplementary Discussion for the details). Thus, qualitatively speaking, the microfiber lamellas with small and large deviation angles provide strength and toughness for this twisted plywood structural material, respectively. According to our experiments (Fig. 3 and Supplementary Fig. 14) and previous reports [3,6,31,34], helical layered structural material can form complicated helicoidal fracture pattern in the failure process. For small layer deviation angle, the helicoidal fracture pattern and interlayered coupling effect can further enlarge the crack resistance and toughness. Consequently, the biomimetic twisted plywood structural material (such as 10° twisted specimen) achieves excellent mechanical performances, superior to many natural, biomimetic and engineering materials (Fig. 5) [9,13,15,16,34-45]. In particular, the biomimetic material exhibits relatively matched mechanical performances and compositions relative to natural cortical bone, making it promising for biomedical application, such as bone substitution.

It is noteworthy that, though the well-developed but costly carbon fibers (CF) have also been arranged into highly ordered or helicoidal structure by conventional engineering manufacturing technique for preparing high-performance carbon fiber reinforced plastics (CFRP) materials [46,47], there are essential differences between the CFRP and our materials presented here. CFRP materials (fabricated by integrating polymer matrix with continuous tows which consist of several thousand individual continuous carbon fibers with diameter of 5-10 micrometers bundled together) belong to traditional engineering materials that possess the structural features with much larger scale compared with that of sophisticated natural materials assembled from nanoscale building blocks. In contrast, our materials presented here focus on using 1D
micro/nanometer-sized building blocks (with scale close to that in natural materials) to imitate nature’s principle and fabricate advanced composite materials with greatly improved properties compared with those of their fundamental compositions (Fig. 5a) due to the high level of ordering of the micro/nanoscale building blocks [8,14]. It has been predicted that combining biomimetic micro/nanostructural control with various artificial synthetic compounds will be possible to propel the development of advanced structural materials, even breaking the performance limits of existing engineering materials. However, precise micro/nanostructural control in large-scale materials remains exceedingly challenging for conventional engineering manufacturing technique [8,13], which partly encourages new explorations including this research.

CONCLUSION

In this study, by developing a novel and efficient bottom-up assembly strategy, high-performance biomimetic twisted plywood structural materials that highly resemble natural hierarchical structures and toughening mechanisms were successfully created in macroscopic bulk form from 1D micro/nanoscale building blocks under mild condition. The resultant materials exhibited controlled and optimal mechanical performances, superior to their fundamental compositions, many natural and man-made structural materials, through precisely engineering the arrangements of 1D micro/nanofibers following nature’s principle at multiscale. Our research here gives promising insights into how to improve the mechanical performances of structural materials from the perspective of biomimetic design featured by micro/nanoscale building blocks, multiscale design, environmental friendliness and mild condition. The proposed material-independent, scalable assembly strategy allowing for precise micro/nanostructural control at macroscopic 3D level, along with reliable theoretical simulations would offer a promising pathway to design many more high-performance 1D micro/nanofiber-based biomimetic structural materials that are expected to exceed existing engineering materials.
METHODS

Preparation of 1D micro/nanoscale building blocks

Hydroxyapatite microfibers were prepared by a modified previous report [48]. In a typical process, 1.33 mL of HNO$_3$, 7.9345 g of Ca(NO$_3$)$_2$·4H$_2$O, 2.6410 g of (NH$_4$)$_2$HPO$_4$ and 11.8140 g of CH$_3$CONH$_2$ were dissolved in 400 mL of deionized water (DIW) and the pH was adjusted to ~3 through HNO$_3$ and NH$_3$·H$_2$O, then the solution was experienced hydrothermal processing with 500 mL autoclave at 180°C for 8 h, and cooled naturally to room temperature. The resultant white product was collected by filtration, washed three times with DIW quickly and dried in a 80°C oven overnight. Ag nanowires and xonotlite nanowires were prepared according to previous reports [49,50]. Calcium carbonate whiskers were commercially available in Shanghai Kai She Feng Industrial Co., Ltd., China.

Fabrication of HA microfibers-sodium alginate (SA) films

SA powder was dissolved into DIW to obtain 2 wt.% SA solution, then the solution was centrifuged (8000 rpm, 10 min) to remove the solid impurities. HA microfibers and SA were blended together in certain ratios under vigorously stirring for 2 h, followed by ultrasonic treatment and vacuum-pumping to remove the air bubbles. For large-area composite films with unidirectional arrangement of HA microfibers, commercially available hair brush adsorbed with HA-SA materials systems was sliding (~2 cm s$^{-1}$) on the hot (~110°C) planar substrate along a certain direction. For large-area composite films with helical/twisted arrangement of HA microfibers, hair brush adsorbed with HA-SA materials systems was sliding (~2 cm s$^{-1}$) on the hot (~110°C) planar substrate by programmed and continuous brushing with each brushing process twisting a predefined deviation angle (Note that the second brushing process was applied until the solvent in the first layer was completely evaporated.). After heat-induced solvent evaporation, HA microfibers orderly arranged films were obtained. The thickness of 2D film can be controlled through adjusting continuous brushing times. The disordered film was prepared by heat-induced
solvent evaporation of HA-SA materials systems in large glass container directly. Ca$^{2+}$ crosslinked HA-SA films were prepared by immersing films into CaCl$_2$ solution (1 mol L$^{-1}$) for 2 h and drying in a 80°C oven for 6 h.

**Fabrication of HA-SA 3D bulk materials**

1 wt.% chitosan (CS) solution was prepared by dissolving 1 g of CS powder in 98 mL of DIW and 1 mL of glacial acetic acids, the solution was centrifuged (8000 rpm, 10 min) to remove the solid impurities. The obtained HA-SA 2D films were cut into smaller pieces with equal size and spray-coated with a thin layer of CS solution on their surfaces, then they were flexibly laminated together, and subsequently were pre-pressed with ~2 MPa at 60°C for 24 h. After that, these prefabricated parts were immersed into CaCl$_2$ solution (1 mol L$^{-1}$) for 2 h and rinsed with DIW. At last, a second hot-pressing with ~40 MPa was applied at 80°C for 24 h.

**Polarized light characterization of ordered structure**

A little of HA single-crystal microfiber powder was slightly spread on the glass slide, another glass slide was then covered. The sample was placed on the object stage of optical microscope (OLYMPUS) between polarizer and polarization analyzer, and was gradually rotated from 0° to 90°. During this rotation process, the degree of brightness of HA microfiber was recorded successively. For ordered and disordered HA-SA films, UV-Visible spectrophotometer (UV-2600, SHIMADZU) was used, the rotated (from 0° to 90°) samples were located between polarizer and polarization analyzer (Note that, for aligned film, the angle values only represent the rotated angle range (0°-90°) and do not indicate the real-time deviation angle between alignment direction and polarizing directions, because we do not know the direction of polarization of the polarizer prior to experiment.). During rotation process, relatively flat absorbance curves (from 600 nm to 650 nm) were recorded successively by UV-Visible spectrophotometer. Sampling interval was 0.2 nm. In this study, the absorbance at 624-626 nm was measured for further exploring the “birefringence effect” of orderly arranged HA microfibers embedded in SA matrix. Every marker in the corresponding figures was statistic, based on 11 data points between 624 nm and 626 nm.
Samples characterizations

Powders XRD patterns were performed on a PW1710 instrument ($\lambda=0.15406$ nm). Films X-ray diffraction experiments were conducted by MAR 345 X-ray single crystal Diffractometer ($\lambda=0.154179$ nm), which was operated with exposure time 240 s, the distance film-detector 250 mm. The microstructures were observed by field emission scanning electron microscope (SEM, Zeiss Supra 40) at an acceleration voltage of 3-8 kV. Transmission electron microscope (TEM) images were obtained by Hitachi H-7650 at an acceleration voltage of 120 kV. Nano X-ray computed tomography (Nano-CT) experiments were performed with large field of view (65 $\mu$m*65 $\mu$m) at the first-generation synchrotron facility (Beijing Synchrotron Radiation Facility, BSRF), which was conducted with the storage ring operating at 2.5 GeV and the beam current of 250 mA. Film samples were rotated about 150 degree (from -75° to +75°), and 301 sheet projections were collected. The original data were reconstructed using XMReconstructor. Micro X-ray computed tomography (Micro-CT) experiments were performed at the GE Phoenix Nanotom M (Yinghua Inspection and Testing (Shanghai) Co., Ltd.) with exposure time 1000 ms, voltage 100 kV, current 110 $\mu$A. Bulk samples were rotated about 360 degree (from 0° to 360°), and 1500 sheet projections were collected. The original data were reconstructed using phoenix datos|x 2.3.

Mechanical properties testing

The mechanical tests were carried out on universal Instron 5565 A mechanical machine with constant displacement mode using 500 N load cells. For 2D films, tensile mode was used. The specimens were cut into ~2 mm wide and ~15 mm long stripes. Tests were performed with a gauge length of 8 mm at a loading rate of 1 mm min$^{-1}$. For 3D bulk materials, three-point bend mode was used. The specimens were carefully cut with size of 2 mm*2 mm*20 mm. Tests were performed with a support span of 12.5 mm at a loading rate of 0.2 mm min$^{-1}$. For single-edge notched bend (SENB) tests, the specimens were first notched to about half of its width through using a 150 $\mu$m-thick diamond raw, and sharpened by repeatedly and slightly sliding a razor blade, the final notch radius is about 50 $\mu$m. SENB tests were performed at a constant loading rate of 1 $\mu$m s$^{-1}$. 
Mechanical calculation

Fracture toughness, $K_{ic}$, was calculated with the following equations [12,13,15].

$$K_{ic} = \frac{P_{ic}S}{BW^{3/2}} f(a/W)$$  \hspace{1cm} (1)

$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W)(2.15 - 3.93a/W + (a/W)^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}}$$  \hspace{1cm} (2)

where $P_{ic}$ is the maximum load value in SENB test, $S$ is support span, $B$ is the thickness, $W$ is the width, $a$ is the initial notch depth of the specimen.

Fracture toughness, $K_{jc}$, was calculated based on $J$-integral calculation method (containing both the elastic and plastic contribution), which is similar to previously reported method for evaluating the properties of other natural and artificial composites [12,13,15,18,51].

$$J = J_{el} + J_{pl}$$  \hspace{1cm} (3)

$J_{el}$ is the elastic contribution based on linear elastic fracture mechanics.

$$J_{el} = \frac{K_{ic}^2}{E'}$$  \hspace{1cm} (4)

The plastic part $J_{pl}$ can be calculated using the following equation,

$$J_{pl} = \frac{2A_{pl}}{B(W - a)}$$  \hspace{1cm} (5)

Where $A_{pl}$ is the area of plastic zone underneath the load-displacement curve.

Herein, $J$ values can be transformed into $K$ values (stress intensity factor) by the following equations,

$$K_{jc} = \left(JE'\right)^{1/2}$$  \hspace{1cm} (6)

$$E' = E(1 - v^2)$$  \hspace{1cm} (7)

Where, $E$ is Young’s modulus, $v$ is the Poisson’s ratio. Because the variation of $E$ only influence $K_{jc}$ with fairly limited way, thus $E'$ was replaced by $E$. 
Crack extension parameter, $\Delta a$, was calculated according to previously reported recursion method [12,13,15,51] with the following equations,

$$a_n = a_{n-1} + \frac{W - a_{n-1}}{2} \frac{C_n - C_{n-1}}{C_n}$$

…………………………………………………

$$C_n = \frac{u_n}{f_n}$$

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$$\Delta a = a_n - a$$

Where $a_n$ and $C_n$, $u_n$ and $f_n$ are the crack length and complaisance, displacement and load at each point after the crack propagation, respectively. $W$ is the width of the specimen.

**Computational methods**

Finite element method (FEM) simulations and molecular dynamics (MD) simulations were performed under uniaxial tension mode. Uniaxial tension simulations can be used to reveal the inherent mechanical behaviors of materials due to that most elements in the specimen of three-point bending experiments are under the uniaxial tension state. FEM simulations were performed to understand the failure mode of this twisted plywood (Bouligand-type) structural HA-SA bulk material under uniaxial tension. As a comparison, we built two FEM models with non-helical (unidirectional) (Fig. 3j) and helical (twisted plywood structural) (Fig. 3h) HA microfiber arrangements, respectively. We performed MD simulations to investigate the tension behavior of the helicoidally stacked microfibers with successive layers. All MD simulations were performed using LAMMPS program [52]. In every single layer, the array of closely adjacent microfibers can be regarded as a lamellae. Each microfiber was modeled as a series of beads connected by harmonic springs [5]. The tension deformation (bond interactions between pairs of atoms) and beading deformation (angle interactions between triplets of atoms) of a single microfiber were modeled by the inter-bead springs and angular springs, respectively. More detailed computational methods can be found in the Supplementary data.
SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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REFERENCES

44. Cruz F. Fabrication of HA/PLLA composite scaffolds for bone tissue engineering using additive manufacturing technologies. *Biopolymers: InTech* 2010.
Figure 1. Brushing-induced assembly for flexibly aligning 1D micro/nanofibers and structural characterizations. (a) Schematic illustration of the brushing-induced assembly method for aligning HA microfibers on heated substrate. (b) SEM image showing the surface of HA-SA film with unidirectionally aligned HA microfibers, yellow arrow denotes brushing direction. Inset is digital image of film. Scale bars, 50 μm and 5 cm (inset). (c) Nano-CT image of HA-SA film with unidirectionally aligned HA microfibers. Scale bar, 10 μm. (d) Absorbance curve of HA-SA film with unidirectionally aligned HA microfibers, showing typical peak value due to birefringence effect. Note that the angle values labelled on the abscissa only represent the rotated angle range (0°-90°) of aligned film and do not indicate the real-time deviation angle between alignment direction and polarizing directions. When the aligned film was rotated to around 45°, the peak value of absorbance appeared. Actually, the deviation angle between alignment direction and polarizing direction (one of the two polarizers) was around 0° rather than 45° at this moment, demonstrating the largest absorption. (e) X-ray diffraction pattern of HA-SA film with unidirectionally aligned HA microfibers. (f) Schematic illustration showing programmed and continuous brushing procedure with each brushing process twisting a predefined deviation angle for designing complicated twisted plywood structural film. (g) Cross-sectional SEM image of the obtained HA-SA film prepared by programmed and continuous brushing procedure, showing obviously twisted plywood structure. Various colored arrows represent gradually twisted microfiber lamellas. Scale bar, 20 μm. (h) Cross-sectional SEM image of xonotlite nanowires (20 wt.%)-SA composite film prepared by continuous and crossed brushing procedure, showing ~90° cross-stacked xonotlite nanowires in SA matrix. Scale bar, 2 μm. (i) Cross-sectional SEM images of xonotlite nanowires (20 wt.%)-SA composite film prepared by programmed and continuous brushing procedure with each brushing process twisting a predefined ~30° deviation angle, showing distinct periodically helical structure. Scale bars, 20 μm and 2 μm.
Figure 2. Biomimetic design of macroscopic 3D twisted plywood structural materials and mechanical investigation. (a) Schematic illustration and digital photographs showing high-efficient “brushing-and-laminating” strategies for flexibly fabricating biomimetic macroscopic 3D bulk materials \((k)\) represents thickness of each lamella resulted from one brushing process, \(m\) represents continuous brushing times for 2D film, \(n\) represents number of laminated films). (b) Comparison of flexural strength and modulus of the obtained 3D bulk materials with five different designed structures. (c) Comparison of fracture toughness of the obtained 3D bulk materials with five different designed structures. (d-i) R-curves of the 3D bulk materials prepared by \(0^\circ\) (bend direction is perpendicular to the longitudinal axis of HA microfibers) (d), \(~10^\circ\) (e), \(~20^\circ\) (f), \(~45^\circ\) (g), \(~90^\circ\) (h) and \(0^\circ\) (bend direction is parallel to the longitudinal axis of HA microfibers) (i) twisted stacking-up styles, respectively. Note that black arrows in (d-i) indicate the precast notch (of the samples) which will initiate crack extension under three-point bending loading condition.
Figure 3. Analyses of crack propagation and toughening mechanisms. (a) Schematic illustration showing the ideal crack extension in typical natural twisted plywood structure. Black arrows indicate the crack extension direction (top-to-down), black lines denote the crack propagation direction in each fiber lamella. (b) SEM image reveals that crack propagation path in the artificial twisted plywood structural material is nearly parallel to the axial direction of HA microfibers and deflects among adjacent HA-SA layers. Black double arrows indicate the actual twisted crack propagation direction in each layer. Scale bar, 5 μm. (c-e) SEM images showing the complicated twisted main crack (c, d) and microcracks ahead of crack tip (e) in the biomimetic twisted plywood structural material. Yellow arrow in (d) indicates crack propagation direction near the notch. Yellow arrows in (e) indicate the microcracks. Scale bars, 20 μm, 50 μm and 10 μm. (f) SEM image showing crack trend in the 3D bulk material with unidirectionally aligned HA microfibers (bend direction is parallel to the longitudinal axis of HA microfibers). Yellow arrow indicates the main crack propagation direction near the notch. The crack is relatively straightforward, and obviously different from that of twisted plywood structural materials. Scale bar, 50 μm. (g) Comparison of fracture toughness of unidirectional and twisted plywood structural materials. (h-k) Comparison of simulated failure modes (damage morphologies) for the twisted plywood structure (θ = 5°) (h, i) and unidirectional structure (θ = 0°) (j, k). The pale brown bars and translucent regions present HA microfibers and SA matrix, respectively. The regions colored in wine denote the damage morphologies of the two structures under uniaxial tension, which can reflect the difference of fracture propagations found in experiments.
Figure 4. Theoretical simulations for crack propagation and deformation mechanisms. (a-d) MD simulations of unidirectional microfiber lamellas with 5°, 20°, 40°, 80° deviation angles (between longitudinal axis direction of microfiber and tension direction), respectively, under the uniaxial tension. When the deviation angle is 5° (a), the deformation mode is rotation. The structural snapshots are colored by the height of the thickness of the established model. Black double arrow shows the loading direction. When the deviation angle is 20° (b), the typical rotation deformation is found. When the deviation angle is 40° (c), the shear deformation can be found. When the deviation angle is 80° (d), the deformation mode is delamination. (e-h) MD simulations of helicoidally stacked microfibers with successive layers (the deviation angle of adjacent microfiber layers is 20°). Rectangular black area in (g) shows different deformation styles for different oriented layers. The blue line surrounded area in (g) shows delamination and bridging. The black arrow in (h) indicates different layer, blue lines in (h) show various fibers orientations due to the complicated deformation styles. The raised crack and its propagation in (g) are mainly due to the delamination of lamellas with large deviation angles. The blue lines in (h) denote the local orientations of microfibers near the crack, demonstrating that the crack penetration perpendicular to the film is impeded by the twisted plywood structure and the local deformation of microfibers. Details are attached in Supplementary Figs 15-19.
Figure 5. Comparison of mechanical properties of the biomimetic HA-SA twisted plywood structural material with various natural and man-made structural materials. (a) Ashby diagram of fracture toughness and modulus for the biomimetic HA-SA material and a wide range of natural structural materials. (b) Ashby diagram of flexural strength and modulus for the biomimetic HA-SA material and various HA-based natural and artificial composites. It can be found that mechanical performances of the biomimetic HA-SA material are superior to those of many natural and HA-based biomedical materials. Particularly, all the strength, modulus and fracture toughness of the biomimetic HA-SA material are similar to those of cortical bone. (c) Ashby diagram of specific strength and specific toughness for the biomimetic HA-SA material and a wide range of artificial and engineering structural materials.