

## Emerging artificial Bouligand-type structural materials

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Until now, the demand for lighter, stronger, tougher and more wear-resistant materials has remained unmet for diverse applications, as many structural materials prepared by traditional engineering manufacturing techniques seem to be approaching their performance limits [1]. Natural biominerals, although composed of relatively brittle minerals such as calcium carbonate and -phosphate or glass and a small amount of ductile biopolymers, always achieve excellent mechanical properties due to their hierarchically ordered architectures and sophisticated interfaces. Thus, biomimetic designs using abundant artificial synthetic units under mild conditions are increasingly considered as viable ways to devise new-style high-performance structural materials that are expected to exceed existing engineering structural materials [2,3].

Many biological composites including fish scale, bone and shrimp dactyl club have partly evolved with unique Bouligand-type structures with hierarchically ordered alignment of micro/nanofibers [1,4]. They are ingenious natural fiber-reinforced materials with excellent damage tolerance that is a highly needed yet unmet mechanical parameter for engineering applications such as aerospace engineering. Compared with the costly carbon-fiber-reinforced composites (CFRPs) produced by complicated processes and harsh conditions, comprehensive imitation of natural fiber-reinforced composites, which feature fine micro/nanoscale

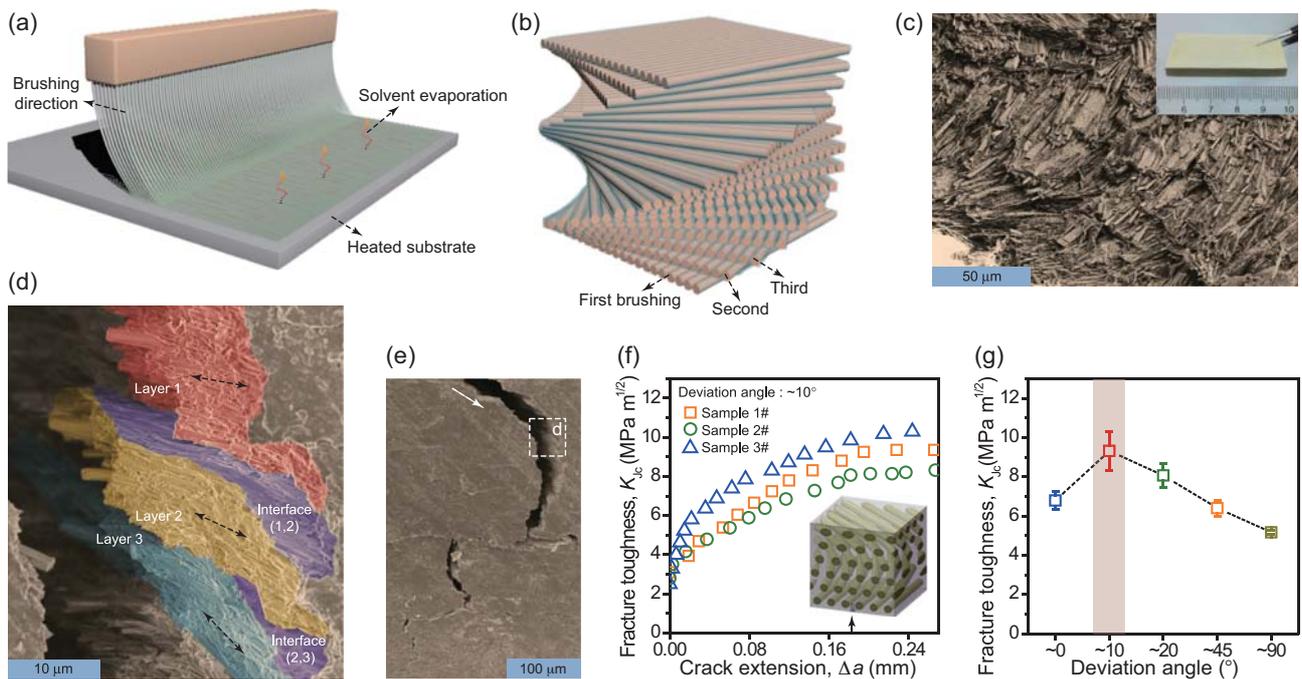
building blocks, multiscale structural design as well as mild and eco-friendly synthetic conditions, is worth considering to meet the demands of sustainable materials.

In a recent report by the research group headed by Shu-Hong Yu from the University of Science and Technology of China (USTC), the researchers proposed a programmable and scalable 'bottom-up' assembly strategy (brushing-and-laminating) for fabricating high-performance biomimetic twisted plywood structural composites in macroscopic bulk form [5], inspired by the twisted plywood (Bouligand-type) structure of *Arapaima gigas* scales [4]. The novelty of this method mainly lies in simple, up-scalable and flexible brushing processes that enable efficient control of the alignment of micro/nanofibers in continuous unidirectional or twisted structural directions (Fig. 1a and b). Based on this method, various 1D building blocks, including hydroxyapatite microfibers, can be aligned (Fig. 1c). Through multilevel regulation of the fiber alignment and subsequent lamination of the ordered sheets, the mechanical performance of the resultant materials can be precisely modulated and optimized, outperforming many natural and synthetic structural materials. This demonstrates the potential and the reliability of the proposed assembly strategy.

In natural materials with twisted plywood structures, a crack always tends to propagate with a helicoidal pattern,

because it largely circumvents fibers along their longitudinal direction rather than severing them, leading to high damage tolerance. Surprisingly, although the artificial material presented in this work consists of relatively brittle hydroxyapatite microfibers and a ductile sodium alginate matrix, it achieves excellent crack characteristics, R-curve behavior and fracture toughness (Fig. 1d-g). To some extent, the artificial counterpart replicates natural hierarchical structures and toughening mechanisms, exhibiting excellent mechanical performance comparable or superior to that of the fundamental constituents and many other natural, artificial and engineering materials.

In short, in contrast to the costly and environmentally threatening production and application of CFRPs, Prof. Yu's group at USTC proposed a programmable and scalable 'brushing-and-laminating' assembly strategy for preparing new-style 3D bulk fiber-reinforced composites from 1D micro/nanoscale building blocks, inspired by natural twisted plywood structures. This assembly strategy allows precise micro/nanoscale structural control to create high-performance bio-inspired structural materials in bulk, which provides insight into micro/nano-size effects on the mechanical properties of macroscopic materials. This highly inspiring work partly narrows the gap between micro/nanoscale biomimetic design and future engineering fabrication, and opens up an avenue for designing



**Figure 1.** Biomimetic design of artificial twisted plywood structural material and characterization. (a) Brushing-induced assembly strategy for aligning micro/nanofibers. (b) Programmable and continuous brushing procedure with each brushing process twisting a predefined deviation angle for designing a complicated twisted plywood structure. (c) The obtained biomimetic material prepared by the flexible brushing procedure, showing obviously twisted plywood structural characteristics similar to the natural archetypes. Inset is the actual biomimetic bulk material. (d) Crack propagation in the artificial twisted plywood structural material is nearly parallel to the longitudinal direction of microfibers and deflects among adjacent fiber lamellae. Black double arrows indicate the actual twisted crack propagation direction in each lamella. (e) Long-range twisted main crack. (f) R-curves of biomimetic bulk material prepared by  $\sim 10^\circ$  twisted stacking-up style. (g) Comparison of fracture toughness of the obtained bulk materials with  $\sim 0^\circ$ ,  $\sim 10^\circ$ ,  $\sim 20^\circ$ ,  $\sim 45^\circ$  and  $\sim 90^\circ$  twisted stacking-up style, respectively. Reprinted from Ref. [5] with permission of Oxford University Press.

many more advanced biomimetic micro/nanofiber-reinforced materials for practical applications.

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