Liquid Crystal Self-templating Approach to Ultrastrong and Tough Biomimic Nanocomposites

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Background

Materials with both high strength and toughness are in great demand for a wide range of applications, requiring strict design of ingredients and hierarchically ordered architecture from nano- to macro-scale. Nacre achieves such a target in the long natural evolution by alternative alignment of inorganic nanoplatelets and biomacromolecules. To mimic nacre, various strategies were developed, approaching nacre-comparable performance in limited size. How to remarkably exceed nacre in both property and size is a key issue to further the advancement of composites. Here we present liquid crystal self-templating methodology to make the next generation of ultrastrong and tough nacre-mimics continuously. The hierarchically assembled composites show the highest tensile strength (652 MPa) among nacre mimics, five to eight times as high as that of nacre (80-135 MPa), and excellent ductility with toughness of 18 MJ m^{-3}, one to two orders of magnitude greater than that of nacre (0.1~1.8 MJ m^{-3}).

Results

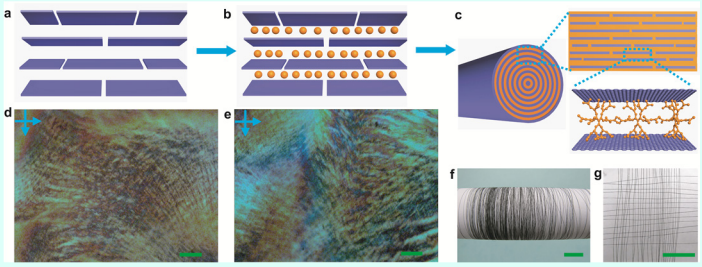

Figure 1. Schematic illustration of LCST strategy and the resulting composite fibres. (a-c) LCST protocol to prepare host-guest layer-structured composites; (d,e) POM images of host GGO LCs (d) and host-guest complex GGO-HPG LCs (e) loaded in the planar cells with concentration of 4 mg mL^{-1}. (f,g) Photographs of a thirty metres long GGO-HPG fiber (f) and a mat of GGO-HPG fibres made by hand (g). Scale bars, 300 μm (d,e) and 1cm (f,g).

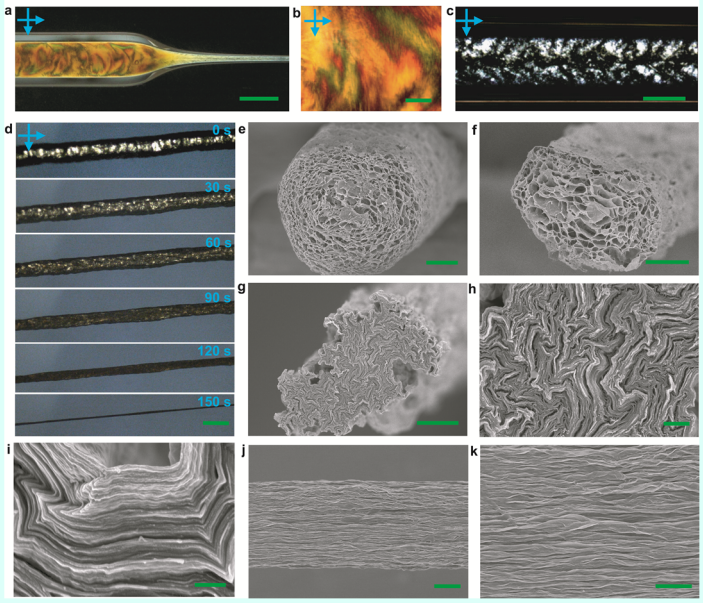

Figure 2. Structural changes of GGO-HPG during spinning. (a) Photograph of GGO-HPG spinning solution inside the glass spinning head under crossed polarizers. (b-d) POM images of GGO-HPG spinning solution in the capillary (b), at the spinning nozzle (c), and the drying procedure of GGO-HPG fiber (d). (e-k) SEM images of cross-section of a GGO-HPG gel fiber at coagulation time of 0 min (e), 3 min (f), and dried fiber (g-i), the surface morphology of the resulting fiber (j,k). Scale bars, 5 mm (a), 500 μm (b), 250 μm (c), 100 μm (d), 30 μm (e), 25 μm (f), 3 μm (g,k), 500 nm (h),250 nm (i), and 5 μm (j).

Table 1. Electrical Conductivities and Mechanical Properties of RGG-HPG Fibers.

Reducing agent	Conductivity (S m^{-1})	Tensile Strength (MPa)	Strain (%)	Toughness (MJ m^{-3})	Young's modulus (GPa)
N_2H_4•H_2O	244	42	2.6	0.6	2.5
Vc	1165	429	4.0	9.3	14.3
Modified Vc	2585	533	5.1	14.4	14.4
HI	3209	443	5.6	14.0	10.8
HI+AcOH	5261	487	3.5	9.5	17.6
200 ºC	41	487	5.9	15.3	10.8

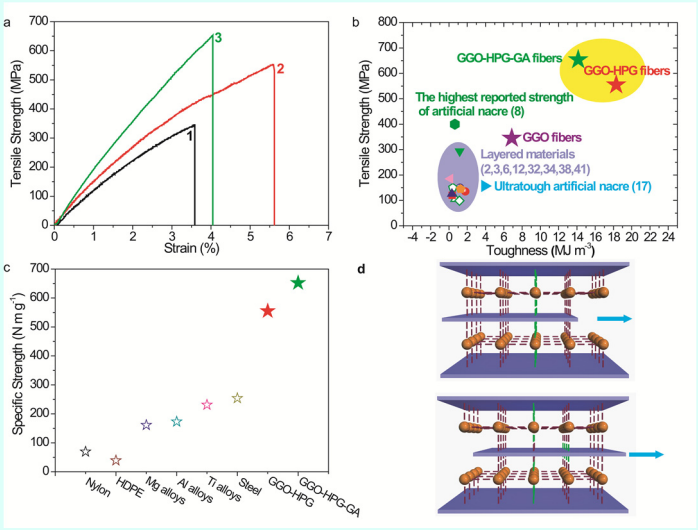

Figure 3. Mechanical properties of fibers. (a) Typical stress-strain curves for neat GGO (1), GGO-HPG (2), and GGO-HPG-GA (3) fibers. (b) Comparison of our bio-mimetic composites with nacre, bone, and reported layer-structured nanocomposites in terms of σ and volumetric toughness. (c) Comparison of our bio-mimetic composites with typical metallic alloys and engineering plastics in terms of specific strength. (d) Schematic illustration of the adaptive hydrogen bonding networks in GGO-HPG composites. The hydrogen bonds (marked in green) are destructed under tension and reformed subsequently as graphene sheets slip (shown in the below scheme).

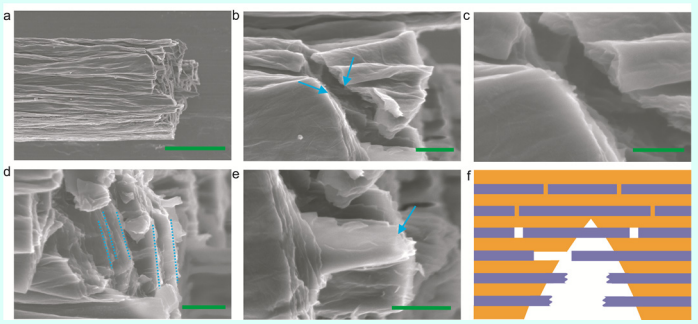

Figure 4. Morphology of fracture section of GGO-HPG fibers. (a-e) SEM images of fracture surfaces of GGO-HPG fibers at different magnification. (f) Deformation mechanism model of GGO-HPG fibers under tensile stress. Scale bars, 5μm (a) and 500 nm (b,d,e), 250 nm (c).

Conclusions

In summary, we designed a green, simple, general, fast and efficient LCST strategy to fabricate the next generation of continuous, ultrastrong and tough bio-mimetic composites. Despite of the mechanical blending process, phase separation between nanofillers and polymer was avoided, even at the case of high content of nanoparticles (~77 wt%). The uniform, regular arrangement and the high aspect ratio of GGO sheets together with the hierarchical structures of our composites led to a large improvement of mechanical performance for nanocomposites. The bio-inspired composites set a new record σ (~0.65 GPa) and toughness (~18 MJ m^{-3}) among nacre mimics. In addition, the composites exhibited high electrical conductivity (5261 S m^{-1}) that was comparable to neat graphene papers. Such multifunctional bio-inspired composites have wide applications in functional textiles as well as flexible and wearable devices. The LCST strategy can be readily extended to prepare other hierarchically structured composites that can be hardly accessed by previous protocols, opening the avenue to multifunctional, highly ordered and tailor-made materials.

References

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Acknowledgments

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