

Mimicking nature at multiple scales

Helmut Cölfen 

Physical Chemistry, Department of Chemistry, University of Konstanz, Universitätsstraße 10, Box 714, D-78457 Konstanz, Germany

Nacre-like ceramics have received an intense focus from the structural material community because the inherently low damage resistance of ceramics, which is a fatal deficiency of ceramics as reliable load-bearing material. It can be improved through nacre-inspired structural designs, i.e., the “brick-and-mortar” structure with alternating soft and hard layers on the microscale. Several technologies have been developed to produce nacre-like ceramics, including freeze casting [1], magnetically assisted slip casting [2], laminating [3] and biomimetic mineralization [4]. The obtained artificial ceramics can exhibit extraordinary anti-fracture behavior without introducing a high volume fraction of ductile non-ceramic components causing a drastic strength decrease of the materials. Nevertheless, while the fracture toughness of mollusk nacre (consisting of 95 vol.% aragonite and 5 vol.% organics) can be 40 times higher than that of pure inorganic aragonite, the toughness amplification of nacre-like ceramics is still notably inferior (Fig. 1(d)) [5]. In fact, the primary reason for the much lower toughness amplification of the nacre-like ceramics lies in the insufficient structural control of these materials [6].

Thus, the question arises how to create nacre-like ceramics with better performance, given that the state-of-the-art fabrication technologies are still coarse compared with the natural syntheses of mollusk nacre. Mao, Yu and their coworkers at the University of Science and Technology of China recently illustrated for bio-inspired nacre [5], that new discoveries on the toughening mechanisms at the nano- and atomic scale sustain the amazing mechanical properties of biological structural materials [7]. In fact, biological structural materials are essentially hierarchically structured over several length scales; besides the structures at microscale such as the “brick-and-mortar” design in nacre, the structural features of the biological structural materials at nano and even atomic scales are also significant to their macroscopic performance [8].

In this context, Meng et al. [5] designed a novel strategy to improve the fracture toughness of nacre-like ceramics. By means of matrix-directed co-mineralization of magnetite nanoparticles (NPs) and aragonite (Figs. 1(a)–1(c)), they fabricated artificial nacre with magnetite NPs embedded in the aragonite platelets. Notably, the incorporation of the NPs into the platelets displayed no effect on the nacre-like structure of the material. The toughness amplification of this artificial nacre reached 16.1 ± 1.1 , which surpassed that of other ceramics with/without biomimetic structures (Fig. 1(d)). Both the direct observations of the fracture surface and the mercury intrusion porosimetry test revealed more platelet sliding in the NP-incorporated nacre compared with the control group, indicating more pronounced extrinsic toughening

in the NP-incorporated nacre (Fig. 1(e)). Because the platelets in the artificial nacre produced via matrix-directed mineralization are too weak to support the platelet sliding, the elevated platelet sliding was attributed to the higher platelet strength of the NP-incorporated nacre, which had been proven by the nanoindentation tests. Beside the increased platelet sliding, the enhanced platelets also enabled more efficient crack deflection during failure, both of which were the main extrinsic toughening mechanisms in nacre-like materials. Indeed, a positive correlation was observed between the platelet strength and the improvement of the extrinsic toughness (Fig. 1(e)), which was also verified by finite element method simulations. Moreover, the dynamic energy absorption (high-strain-rate compression) and the wear resistance of the NP-incorporated artificial nacre surpass those of the natural nacre specimen, which stem from both the NP-induced residual strain, and the flexibility of the platelets in the artificial nacre.

To explain the increased platelet strength, Meng et al. first excluded three strengthening mechanisms, i.e., the NP-induced grain refinement, the Orowan strengthening and the load transfer strengthening by analyzing the structural features of the artificial nacre. Then they measured the lattice parameters of the aragonite platelet using high-resolution X-ray diffraction analysis. The lattice contraction suggested an additional compressive residual stress in the aragonite due to NP incorporation (Fig. 1(f)). This is similar to lattice stress/strain as additional mechanism to increase the strength and toughness of some Biominerals [7, 9].

In addition, a counteracting tensile residual stress was found in the NPs (Fig. 1(g)). As a result of the compressive stress field in the aragonite lattice, an additional external tensile force is needed to break the platelet, leading to a net platelet strengthening. Moreover, the intrinsic toughness of the artificial nacre incorporated with NPs also increased, because the crack initiation and even propagation were retarded by the compressive stress field in the platelets.

Strength and toughness, both of which are favorable for structural materials, are unfortunately not compatible with each other in many conventional materials. The exciting result reported by Meng et al. demonstrated that, with the merit of the nacre-mimetic design at microscale, platelet strengthening through a bio-inspired mechanism at nanoscale can effectively improve the overall fracture toughness of artificial nacre through extrinsic mechanisms. This not only provides a promising strategy to break the bottleneck of the limited toughening amplification of biomimetic ceramics (Fig. 1(d)) but also reveals that the pursuit of higher strength or higher toughness does not necessarily require to compromise each other. A similar strategy can be facilely executed

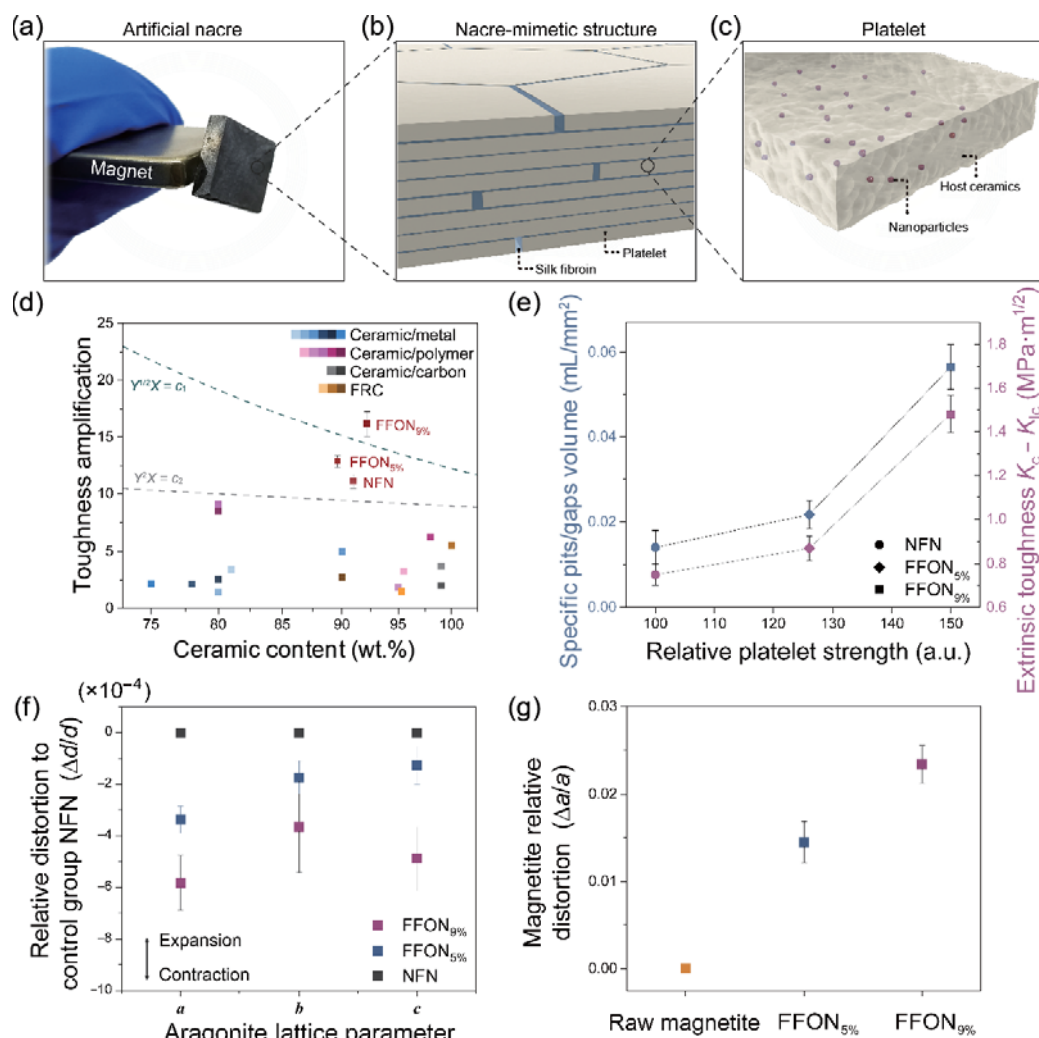


Figure 1 (a)–(c) Schematics of the synthesis process of nanoparticle incorporated artificial nacre (FFON) with 5 resp. 9 wt.% of incorporated magnetite nanoparticles. (a) Black-colored FFON_{9%} adsorbed to a magnet. Schematic illustration of the (b) nacre-mimetic structures and (c) the aragonite platelet with incorporated nanoparticles. (d) Ashby diagram of the toughness amplification versus the main ceramic content for artificial ceramics. FRC = fiber reinforced ceramics. (e) A correlation between specific volume and extrinsic toughness. NFN = sample without magnetite nanoparticles. (f) Relative distortion of aragonite to the control group of artificial nacre without incorporation of magnetite NPs (NFN). (g) Lattice expansion of the magnetite in the artificial nacre with respect to the raw magnetite. Reprinted with permission from Ref. [5], © Wiley-VCH GmbH 2022.

in slurry-based fabrication techniques, such as three-dimensional (3D) printing, to obtain more efficient extrinsic toughening mechanisms by incorporating a suitable secondary incorporated phase into the primary ceramic layers to enhance the platelets via residual stress.

References

- [1] Bouville, F.; Maire, E.; Meille, S.; Van De Moortèle, B.; Stevenson, A. J.; Deville, S. Strong, tough and stiff bioinspired ceramics from brittle constituents. *Nat. Mater.* **2014**, *13*, 508–514.
- [2] Le Ferrand, H.; Bouville, F.; Niebel, T. P.; Studart, A. R. Magnetically assisted slip casting of bioinspired heterogeneous composites. *Nat. Mater.* **2015**, *14*, 1172–1179.
- [3] Gao, H. L.; Chen, S. M.; Mao, L. B.; Song, Z. Q.; Yao, H. B.; Cölfen, H.; Luo, X. S.; Zhang, F.; Pan, Z.; Meng, Y. F. et al. Mass production of bulk artificial nacre with excellent mechanical properties. *Nat. Commun.* **2017**, *8*, 287.
- [4] Mao, L. B.; Gao, H. L.; Yao, H. B.; Liu, L.; Cölfen, H.; Liu, G.; Chen, S. M.; Li, S. K.; Yan, Y. X.; Liu, Y. Y. et al. Synthetic nacre by predesigned matrix-directed mineralization. *Science* **2016**, *354*, 107–110.
- [5] Meng, Y. F.; Zhu, Y. B.; Zhou, L. C.; Meng, X. S.; Yang, Y. L.; Zhao, R.; Xia, J.; Yang, B.; Lu, Y. J.; Wu, H. A. et al. Artificial nacre with high toughness amplification factor: Residual stress-engineering sparks enhanced extrinsic toughening mechanisms. *Adv. Mater.* **2022**, *34*, 2108267.
- [6] Barthelat, F. Designing nacre-like materials for simultaneous stiffness, strength and toughness: Optimum materials, composition, microstructure and size. *J. Mech. Phys. Solids* **2014**, *73*, 22–37.
- [7] Polishchuk, I.; Bracha, A. A.; Bloch, L.; Levy, D.; Kozachkevich, S.; Etinger-Geller, Y.; Kauffmann, Y.; Burghammer, M.; Giacobbe, C.; Villanova, J. et al. Coherently aligned nanoparticles within a biogenic single crystal: A biological prestressing strategy. *Science* **2017**, *358*, 1294–1298.
- [8] Rousseau, M.; Lopez, E.; Stempflé, P.; Brendlé, M.; Franke, L.; Guette, A.; Naslain, R.; Bourrat, X. Multiscale structure of sheet nacre. *Biomaterials* **2005**, *26*, 6254–6262.
- [9] Seknazi, E.; Pokroy, B. Residual strain and stress in biocrystals. *Adv. Mater.* **2018**, *30*, 1707263.