wear properties and high-temperature resistance expected for ceramic materials. Toughening is evidenced by the increasing resistance of the material against crack growth (known as a rising R-curve behaviour; Fig. 2b), and results in the very tortuous crack path observed during fracture of the nacre-like ceramic as compared with unstructured alumina (Fig. 2c). This is quite remarkable considering the fact that the material is made entirely of brittle ceramic building blocks. In fact, the levels of toughness achieved exceed by an order of magnitude than those of advanced ceramics of the same composition and grain size, and are comparable to those of the toughest polymer-infiltrated bulk nacre-like composites reported thus far[2] (Fig. 2a). This indicates that toughening is possible even in the absence of an energy-absorbing polymer phase.

The lack of a polymer phase allows the nacre-like alumina ceramics of Deville and co-authors to maintain their strength and toughness even at 600 °C (Fig. 2b), a temperature that would be sufficient to degrade any organic constituent. Still, the authors' freeze-casting approach could potentially produce all-inorganic lamellar ceramics with unprecedented strength and toughness at higher temperatures by employing inorganic building blocks that are more heat resistant. These materials could extend the lifetime or operating temperature of refractory linings for metallurgical ovens and combustion chambers of aircrafts. By replicating design concepts of a biological material using building blocks with functional properties that are superior to those of natural constituents, Deville and collaborators' work nicely illustrates how bioinspired approaches can lead to materials that easily outperform state-of-the-art technologies[7]. This and other recent examples[8–10] of bioinspired materials design suggest that an increasing number of processing routes that effectively capture the design principles of natural materials are soon expected to emerge. ❐

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References

1. Meyers, M. A., Chen, P. Y., Lopez, M. I., Seki, Y. & Lin, A. Y. M. *J. Mech. Behav. Biomed. Mater.* **4,** 626–657 (2011).
2. Munch, E. *et al. Science* **322,** 1516–1520 (2008).
3. Bonderer, L. J., Studart, A. R. & Gauckler, L. J. *Science* **319,** 1069–1073 (2008).
4. Bouville, F. *et al. Nature Mater.* **13,** 508–514 (2014).
5. Deville, S. *Adv. Eng. Mater.* **10,** 155–169 (2008).
6. Ritchie, R. O. *Nature Mater.* **10,** 817–822 (2011).
7. Studart, A. R. *Adv. Mater.* **24,** 5024–5044 (2012).
8. Erb, R. M., Libanori, R., Rothfuchs, N. & Studart, A. R. *Science* **335,** 199–204 (2012).
9. Erb, R. M., Sander, J. S., Grisch, R. & Studart, A. R. *Nature Commun.* **4,** 1712 (2013).
10. Mirkhalaf, M., Dastjerdi, A. K. & Barthelat, F. *Nature Commun.* **5,** 3166 (2014).
11. Meyers, M. A., Lin, A. Y.-M., Chen, P.-Y. & Muyco, J. *J. Mech. Behav. Biomed. Mater.* **1,** 76–85 (2008).

NATURAL MATERIALS

Armoured oyster shells

The remarkable properties of a bivalve shell that enable it to protect the animal against its predators could inspire the design of new lightweight armour materials.

Robert O. Ritchie

Nature designs materials as hierarchical architectures with complex composite structures spanning the nano to near-macro length scales to create unique combinations of properties that are often difficult to achieve with synthetic materials. Indeed, the quest to understand such amazing natural structures and their intriguing mechanisms has provided a fresh stimulus for the development of new man-made materials with unprecedented properties and performance.

This is particularly evident in the search for superior lightweight armour for use in personal protection and military applications. Nature has been adept at creating lightweight armours for over 500 million years, both as highly flexible dermal armours, for example fish scales, or more rigid shells, such as those of molluscs[1]. Despite wide variations in composition, architecture and structure, there is distinct commonality: bio-armours consist of sets of rigid plates — varying in thickness from several 100 μm for small fish to over 100 mm in the case of dinosaurs — connected by collagen fibres or muscles. Flexibility is generally achieved through the overlapping or juxtaposition of plates. In comparison, Kevlar (aramid fibre)-based synthetic materials[2], which are used in many personal armour applications at present, are not especially lightweight (~20 kg is added to a soldier's load). Hence, there remains considerable insight that could be drawn from studying natural systems for the fabrication of improved synthetic armour materials.

Writing in *Nature Materials*, Li and Ortiz[3] report on the penetration resistance and spatial localization of damage as a consequence of effective energy-dissipation mechanisms in the shell of the bivalve marine mollusc *Placuna placenta*. The translucent optical properties of the outer shell have resulted in its use in window panes as a cheap alternative to glass in parts of Asia, and hence, *P. placenta* is also called the 'window pane' oyster[4]. The key to the shell's defense properties lies in the presence of graded nano/microstructures. Li and Ortiz explain how in the *P. placenta* shell, these graded structures comprise an outer layer to resist and localize penetration damage, and a fracture-resistant base to absorb the excess energy without plate failure. The latter has the effect of maintaining a 'multi-hit' capacity.

The first role of armour is to arrest the penetrating object, which is generally achieved by spatially localizing any comminuted zone directly beneath the penetrator. In man-made armour, this is often achieved through the use of a hard surface layer to minimize local plasticity, in fish scales, for example, it is achieved by a highly mineralized outer layer[1,5], and in abalone shells by a prismatic layer of mineral laths aligned perpendicular to the surface to optimize wear and penetration resistance[6]. The second role of armour is to accommodate the deformation; graded material properties throughout the thickness of the armour are used to ensure that the larger deformations are in the inner regions, which are tough enough to support greater amounts of plastic deformation than the hard, but brittle, outer shell. Fish scales achieve this with a collagen-based inner layer[1,5,7]. Amazingly, in certain fish, lamellae of collagen fibrils are arranged in the form of a spiral staircase (Bouligand) structure;

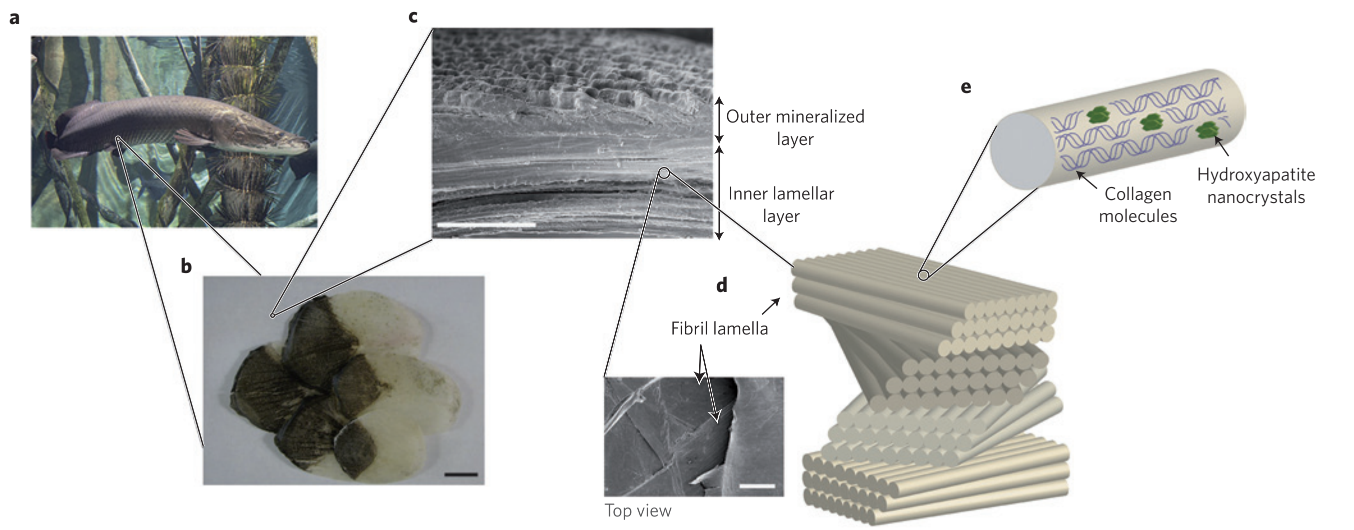

Figure 1 | The armoured protection of *Arapaima gigas* fish scales. **a**, The scales of the *A. gigas* fish act as a natural dermal armour by providing multiple layers of defense against piranha attacks. **b**, The overlapping pattern of *A. gigas* fish scales allows flexibility through bending of multiple scales. Scale bar, 20 mm. **c**, A cross-section of a scale. The scale has graded material properties and consists of a highly mineralized outer shell to provide hardness and a tough inner core of collagen-fibril lamellae. Scale bar, 0.5 mm. **d**, In a unique fashion, the lamellae are arranged in a Bouligand-type (or twisted plywood) pattern, with the fibrils within neighbouring lamellae rotated by various angles. Scale bar, 200 μm. **e**, Each lamella is composed of mineralized collagen fibrils with a predominantly parallel orientation. Under stress, the fibrils tend to align in the direction of the loading to be more effective in carrying the extra load, thereby enhancing the fracture resistance of the scale. Figure reproduced from ref. 7, 2013 NPG.

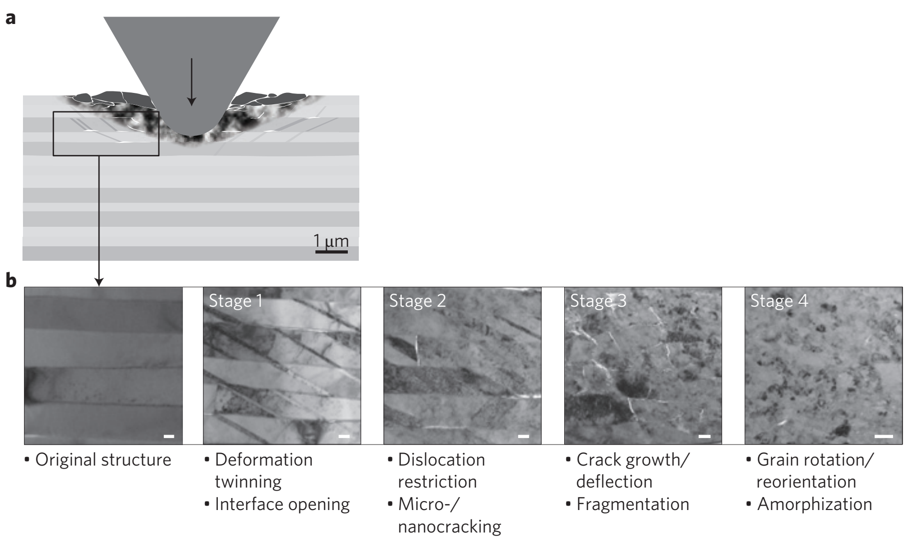

Figure 2 | The containment of penetration damage in the shell of the *P. placenta* bivalve when nanoindented[3]. **a**, A schematic illustration of the application of load (arrow) to the bivalve shell during nanoindentation experiments. **b**, Transmission electron microscopy images that show the deformation structure at different distances from the load (moving towards the indenter, as shown in the images from left to right). The containment of penetration damage in the *P. placenta* shell occurs through the formation of radiating deformation twins. This process then catalyses a series of additional nanoscale inelastic mechanisms that act to absorb the excess strain via crack deflection, constrained nanocracking in and between the calcite bricks, opening-up of the viscous organic interlayers, the formation of nanoscale grains, and the rotation and reorientation of the grains. Note that the damage zone and associated cracking is confined to a few hundred micrometres surrounding the point of penetration. All scale bars, 100 nm.

when stressed the individual collagen fibrils automatically align in the direction of the load to enhance fracture resistance (Fig. 1)[7].

In *P. placenta*, armour resistance is achieved in a similar fashion through the creation of a tiled assembly of 300-nm-thick elongated diamond-shaped crystals of calcite, aligned nominally parallel to the surface of the shell and again separated by organic nanolayers. Li and Ortiz, however, reveal a fascinating new twist in damage localization and energy absorption of natural armours — deformation by nanoscale twinning (Fig. 2). Crystalline materials generally plastically deform by the motion of dislocations, but where this is inhibited, for example, in certain crystal structures or at low temperatures, they can form deformation twins, which are thin, nano/microscale laths with mirror-image atomic arrangements across the twin-boundary interface. Li and Ortiz show that for *P. placenta*, ~50-nm-thick nanotwins form around the penetration zone; these twin bands effectively accommodate the excess deformation and judiciously confine it to a small volume (such that the optical translucency of the shell is preserved) before the twins arrest at the organic interfaces between the calcite crystals. Perhaps more importantly, this twinning process seems to catalyse a series of additional inelastic energy-absorbing mechanisms such as crack deflection, constrained nanocracking in and between the calcite bricks, stretching of the viscous organic interlayers, and the formation and reorientation of new nanograins. Through these intriguing nanoscale processes, the *P. placenta* shell can effectively resist predatory attack by obeying the two principles of armour material: arrest and localize penetration damage and contain the excess deformation without catastrophic fracture.

Not to detract from these findings but a limitation of such studies is whether we can ever mimic such a lightweight structural material in bulk synthetic form to reflect nature's hierarchical architectures and to capture their unique mechanical properties. In this regard, bioinspired functional materials have enjoyed some success so far, such as water-resistant (hydrophobic-coated) materials based on specific plants and adhesive surfaces based on gecko feet[8]. However, structural materials pose a particular challenge because they invariably comprise, as with the bivalve shell, a large fraction of a mineral phase (for hardness) with a minute fraction of bio-organic compliant phase (for ductility and toughness), which makes them especially difficult to make. Several man-made deformation twinning materials do exist although with similar mechanical properties to the bivalve, but they are quite different in structure and definitely not lightweight. A well-known example is Hadfield manganese steels, which are 11–15 wt% Mn steels used in the mining industry in rock crushers because of their hardness and fracture resistance[9]. Similar to the *P. placenta* shell, these steels are deformation twinning materials and as such are capable of exceptional surface abrasion and penetration resistance while maintaining sufficient toughness to prevent fracture. Indeed, they form the basis for a range of new high-Mn steels called twinning-induced plasticity steels[10], which as a consequence of their high strength and ductility have become attractive for automobile applications.

One cannot help but marvel at the scientific endeavour. When Hadfield Mn-steels were developed by Sir Robert Abbott Hadfield in 1883, he was almost certainly oblivious to the way the *P. placenta* shell protects the animal from predators, yet the physical micro-mechanisms are essentially the same. It seems that although the biological and physical sciences are often considered to be orthogonal, they clearly have some things in common. ❐

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References

1. Yang, W. *et al. Adv. Mater.* **25,** 31–48 (2013).
2. Lee, Y. S. *et al. J. Mater. Sci.* **38,** 2825–2833 (2003).
3. Li, L. & Ortiz, C. *Nature Mater.* **13,** 501–507 (2014).
4. Gallardo, W. G. *et al. Biol. Conserv.* **73,** 33–38 (1995).
5. Song, J. *et al. J. Mech. Behav. Biomed. Mater.* **4,** 699–712 (2011).
6. Erb, R. M. *et al. Science* **335,** 199–204 (2012).
7. Zimmermann, E. A. *et al. Nature Commun.* **4,** 2634 (2013).
8. Meyers, M. A. & Chen, P.-Y. *Biological Materials Science* (Cambridge Univ. Press, 2014).
9. Oberg, E. & Jones, F. D. *Machinery's Handbook* 18th edn, 1917 (Industrial Press, 1970).
10. Grässel, O. & Frommeyer, G. *Mater. Sci. Technol.* **14,** 1213–1216 (1998).