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Nanoscale Deformation Processes Revealed in Nacre of *Pinna nobilis* Mollusk Shells

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Overcoming the fundamental tradeoff between toughness, strength, and resilience remains a fundamental design challenge for structural materials [1]. In this sense, the selection and design of modern high-performance structural engineering materials is driven by optimizing combinations of the mechanical properties and requirements for predictable and non-catastrophic failure [2]. Nature has optimized these high-performance materials with unrivaled strength and toughness using 3D hierarchical composite architectures consisting of intimately arranged organic and mineral phases assembled with precision beyond human technology. Among the diverse set of structural biominerals in nature, nacre is the prototypical supermaterial showing fracture toughness (10 $\text{MPa}\cdot\text{m}^{1/2}$) that is 40-fold larger (a factor of ~2,000 in terms of energy) than that of the single crystal/monolithic calcium carbonate from which it is mainly constructed (~0.25 $\text{MPa}\cdot\text{m}^{1/2}$) [1,2]. However, most knowledge of the biomineral toughening process is assembled from microscale tribology, tensile, or compression on bulk specimens [1,3,4]. Understanding nanomechanical responses across the 3D hierarchical architectures is critical to understand how individual nacre components work together to enhance the properties beyond the sum of its parts.

Our investigation of toughening in nacre reveals nanomechanical deformation of organic interfaces, nanocrystallites, and organic inclusions that are key to damage-tolerant nacre. Using high-resolution scanning / transmission electron microscopy (S/TEM) combined with in-situ indentation, we observe two quasi-plastic deformation processes in nacre compression, tablet interlocking and nanograin deformation that absorb energy for toughening yet remains fully recoverable. Annular dark-field (ADF) STEM reveals non-destructive locking of nacre across the organic interfaces such that adjacent inorganic tablets structurally join during heavy compression (Fig. 1a, b). The intra-tablet region also compresses resulting in deformation of organic inclusions. Remarkably, the completely locked interface recovers its original morphology without leaving any damage after compression is released and retains its full mechanical strength (at least up to 80% yield strength) (Fig. 1c, 2e). During compression, aragonite grains and organic inclusions rotate and deform indicating the nanoscale toughening processes in nacre tablets (Fig. 1, insets).

Nacre has mechanical response regimes of high and low compression visible by the change of strain contours in TEM. Low levels of compression generate intra-strain contours propagated within a tablet without penetration to adjacent tablets (Fig. 2a). At higher compression, tablets couple and inter-strain contours begin to spread across its organic boundaries (Fig. 2b). This indicates that biopolymer interfaces confine strain propagation within tablets (intrastrain). Nano-organics within the nacre not only enable quasi-plasticity but also mitigates crack propagation within and between tablets when partial failure begins. We find highly deformed nacre recovers its mechanical strength on the external stimuli up to 80% of the yield stress during consecutive indentations (Fig. 2c). The elastic modulus remained unchanged during eight-consecutive compressions (blue and red). After ~0.8 GPa, the nacre tablet starts to deform quasi-plastically but firmly preserves its initial structure after unloading. Full recovery was also observed in highly deformed nacre so long as crack formation had not begun (Fig. 1).

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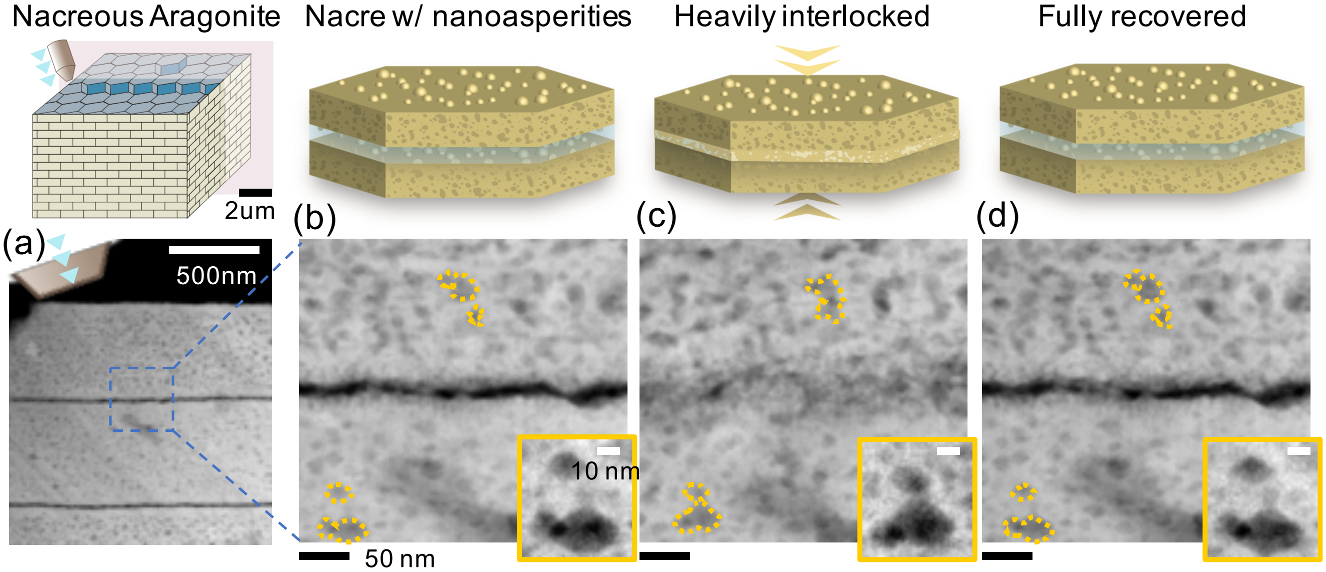

Figure 1. Cross-sectional view of deformation and recovery in nacre. (a) ADF-STEM overview of nacre indentation. (b-d) Higher resolution ADF-STEM showing the interface with nanograins (b), heavily interlocked under 50 µN compression (c), and fully recovered the initial structure (d). Insets demonstrate the movement of nanosized organic inclusions with the inorganic matrix compression accommodating for nanograins to deform avoiding damage.

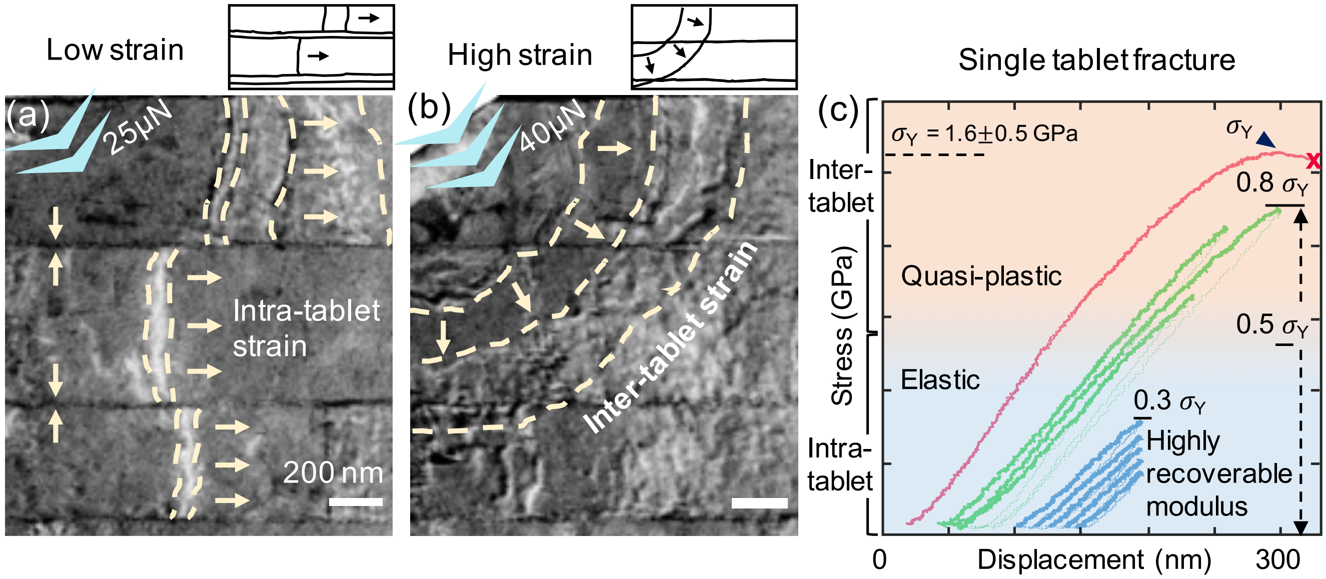

Figure 2. Contrast-inverted TEM of nacre cross-section under (a) low-stress where strain contours propagate within and (b) high stress where tablet strain propagates between tablets. (c) Nine consecutives in situ TEM compressions on the same nacreous tablet demonstrating recoverable mechanical strength of nacre. Three different colors represent different contact areas during the compression tests.