

Interface structure and crystal growth mechanism in Nacre

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Keywords: microscopy, interface, biomaterials, spiral growth, crystal structure

Nacre (mother of pearl), the crown jewel of natural materials, has been studied for over 160 years. As a classical armor material, Nacre is known for its remarkable mechanical strength and toughness, which are superior to that of many synthetic composites. Its extraordinary material properties can be attributed to its highly regular architecture — a brick-and-mortar arrangement of aragonite platelets wrapped in protein and polysaccharide fibers [1]. Mature nacre consists of pseudo-hexagonal aragonite platelets of 5-8 μm diameter and 0.5 μm height that generally are stacked vertically and form horizontal sheets of lamellae. Nacre is comprised of 95% calcium carbonate in the aragonite polymorph with 5% or less organic macromolecules sandwiched in between. This juxtaposition of organic and inorganic elements renders nacre notch insensitive and capable of withstanding substantial inelastic strain, which offers a work of fracture about 3000 times greater than monolithic ceramics. These extraordinary physical properties have attracted much interest from many disciplines. Yet, the precise structural features governing its extraordinary strength and its growth mechanism remain elusive [2].

In this paper, we present a series of observations, using electron, ion, x-ray and atomic force microscopy (AFM), pertaining to Nacre's organic-inorganic interface, organic interlayer morphology and properties, large-area crystal domain orientations, and nacre growth. In particular, we describe unique lateral nano-growths and paired screw dislocations in the aragonite layers, and demonstrate that the organic material sandwiched between aragonite platelets consists of multiple organic layers of varying nano-mechanical resilience. Based on these novel observations and analysis, we propose a spiral growth model that accounts for both [001] vertical propagation via helices that surround numerous screw dislocation cores and simultaneous $\langle 010 \rangle$ lateral growth of aragonite sheet structure. For example, we analyze newly-discovered surface features of the organic layers in nacre using SEM and contact mode AFM (see Figure 1). The organic surface consists of densely packed, globular molecules which are presumably proteins. The organic matrix between the vertical faces of removed aragonite platelets outlines a honeycomb pattern. This pattern is superimposed on the exposed layer of platelets, allowing simultaneous imaging of adjacent layers. We find that vertically adjacent layers of platelets overlap extensively, with three to six platelets from the layer above overlapping with a given platelet. We also observe significant differences between the organic interlayer and the vertical organic matrix between adjacent platelets, which have not been previously documented. The molecules in this matrix have a diameter of $149 \pm 20\text{nm}$ across the layers. In contrast, the vertical organic matrix consists of molecules with a significantly larger diameter of $249 \pm 26\text{nm}$. We then probed the adhesive properties of the vertical and interlayer matrices by measuring the contact force between the AFM cantilever and the sample surface. We identified four surface layers based on height: one consisting of the vertical organic matrix remaining from the overlying layer, as well as three different layers on the top of platelet surfaces. We show that each layer has a distinct adhesive force, ranging from $4.2 \pm 0.2\text{nN}$ at the border region to $18.9 \pm 1.0\text{nN}$ at the bottom layer.

These discoveries can yield insights into the mechanisms of nacre assembly and growth. The extent of vertical overlap between adjacent platelet layers renders any mechanism of vertical continuous growth unlikely, as each of the overlapping platelets can conceivably exhibit different crystal orientations. On the other hand, horizontal penetration of mineral is likely to be facilitated by the higher porosity of the vertical organic layer, which is thinner and is composed of larger molecules. Moreover, the disparate adhesiveness of the different organic layers may be important factors contributing to the ductility and toughness of nacre. These new findings may aid in creating novel organic-inorganic micro/nano composites through synthetic or biomineralization pathways.

1. A.P. Jackson, et al., *Composites Science and Technology* **36** (1989) p255.
2. N. Yao, et al., *Journal of the Royal Society Interface* **6**, (2009) p367.
3. This work was partially supported by the NSF-MRSEC program and the NJCST.

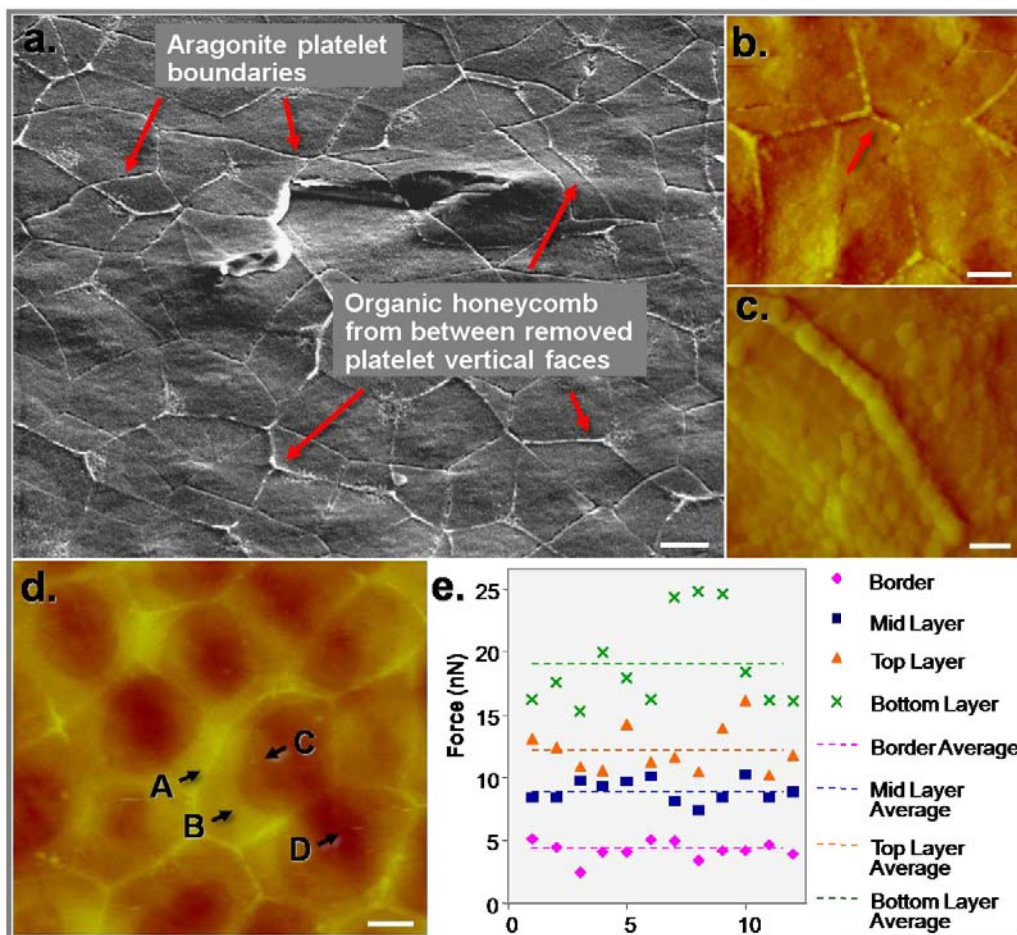


Figure 1. (a) SEM image of the exposed nacre surface, revealing that organic layers from between the vertical faces of the removed aragonite platelets remain and form honeycomb-like outlines, effectively allowing the imaging of platelet boundaries from two adjacent layers at once. Two paired screw dislocation cores can also be seen. AFM images (b) showing honeycomb-like outlines similar to those in (a), revealing in (c) that the outline wall consists of a single layer of molecules with a diameter significantly larger than of those in the surrounding matrix, and (d) demonstrating four surface layers classified by height, marked as A: border, B: top layer, C: middle layer, and D: bottom layer. (e) provides a comparison of experimental data of critical pulling force collected at twelve different locations in those four regions. [Scale bar = 2 μm in (a, b, d), and 500 nm in (c)]