

Contributions of Individual Organic Layers to the Mechanical Properties of Nacre

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The mechanical properties and organization of the inorganic aragonite in nacre have been studied extensively; however, substantially less research exists on nacre's organic layers. Past work on nacre's impressive ability to resist failure have proved that the organic and inorganic layers are ordered in a brick-and-mortar arrangement over orders of magnitude to yield a superior material and the addition of only 5% vol organic material results in a more than 20-fold increase in fracture strength compared to pure aragonite [1]. Still, structure-function relationships in the organic layer remain unclear and limit engineers' ability to create biomimetic layered materials. Our research aims to deconstruct the organic layer in order measure the properties of each layer individually and develop theories regarding the manner by which nacre forms and organizes itself.

Bivalve nacre has been shown to have proteinaceous layers coating each (001) face of the aragonite tablets as well as long chitin strands which form a network spanning the space between tablet layers [2]. In the (010) direction, aragonite tablets are separated by crisscrossing collagen strands which have been imaged in gastropod nacre as well. Previous research by Yao et al. has shown that there are four distinct organic layers in gastropod nacre [3]. AFM contact force measurements performed on these layers have shown that their adhesive force varies from the cleaved surface to the underlying aragonite layer. They found that the boundary layer had the lowest adhesive force followed by the middle, top, and bottom layers respectively. Given our previous understanding of the organic layer as being composed of one layer of chitin sandwiched between two layers of protein, with an additional raised border of collagen, we want to selectively remove layers to determine the nanomechanical properties of each. By removing only one layer at a time, we are able to observe the remaining layers and thereby determine the mechanical properties associated with the missing layer.

In this paper, we systematically removed layers of the nacre surface using plasma etching in order to view the layers underneath. We first imaged our samples using both SEM and AFM. This allowed us to find areas of interest such as screw dislocations, complementary cleaved tiles, and nanoasperities. We then plasma etched our samples in order to remove layers off the surface. We placed a small marker in the center of our sample that could act as an origin for our coordinate system. Because we had recorded the areas of interest on our samples, we could then return to the area that had been imaged previously in order to determine the effect of the etching.

From the AFM images we see that the top organic layer has been etched off to reveal a second layer which still shows aligned imprints from nanoasperities though the ones that remain are deeper and less numerous. This also demonstrates that imprints go quite deep and do not shrink, therefore nanoasperities most likely contact the above tablet to either impart crystal orientation or serve as a toughening mechanism. By utilizing the E-SEM's ability to image nonconductive samples, we are able to analyze an uncoated sample. From the E-SEM image we can see a multitude of miniature holes in the organic layer similar to those in gastropod nacre in addition to the larger gaps in the layer. These could have many important implications for several ongoing research questions regarding structure-function relationships in nacre, including the manner in which crystal orientation passes to aragonite layers separated by

organic material and characterization of individual organic layers. As layers build on top of one another, aragonite crystals nucleate and grow on the underlying proteins. The sizes and locations of pores in the organic layers may yield clues as to how mineral transport occurs between layers. It is also interesting to see that the plasma etch on the E-SEM image shows an edge that is not as clean and continuous, most likely it has begun to enlarge those pores. A future project could therefore go further in relating etch time to layer removal to map the distribution of components in the layers.

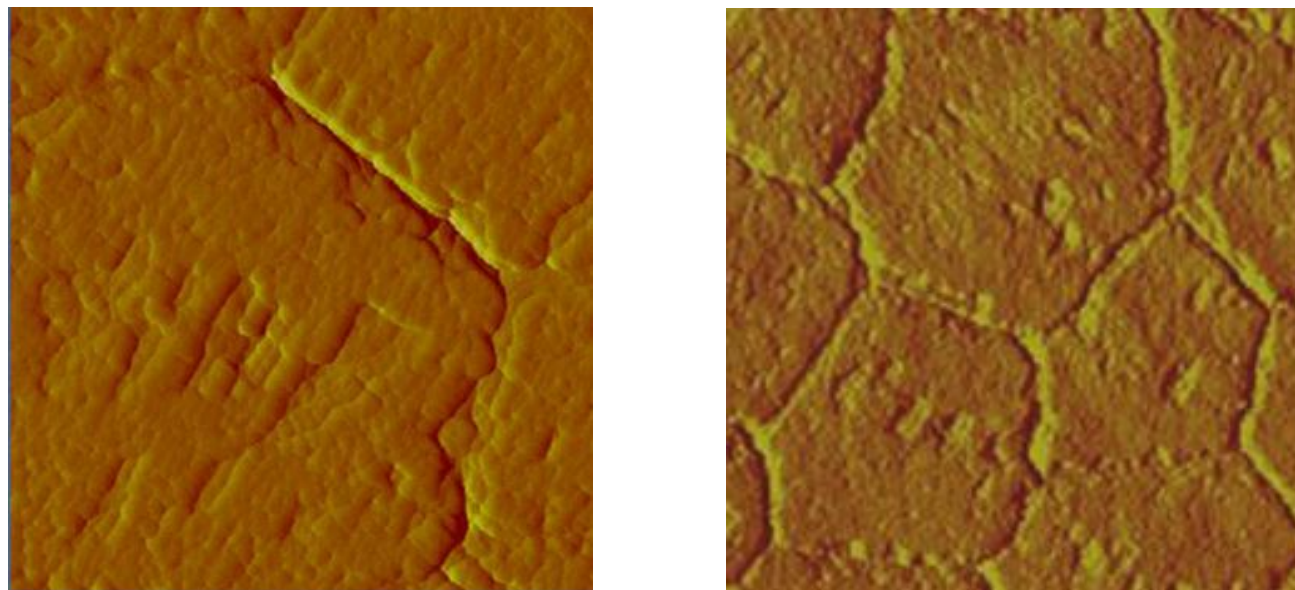


Figure 1 Two AFM images showing similar tablets before and after plasma etching at different magnifications ($4\mu\text{m}$ and $7\mu\text{m}$ respectively) showing that the organic layers have been etched away.

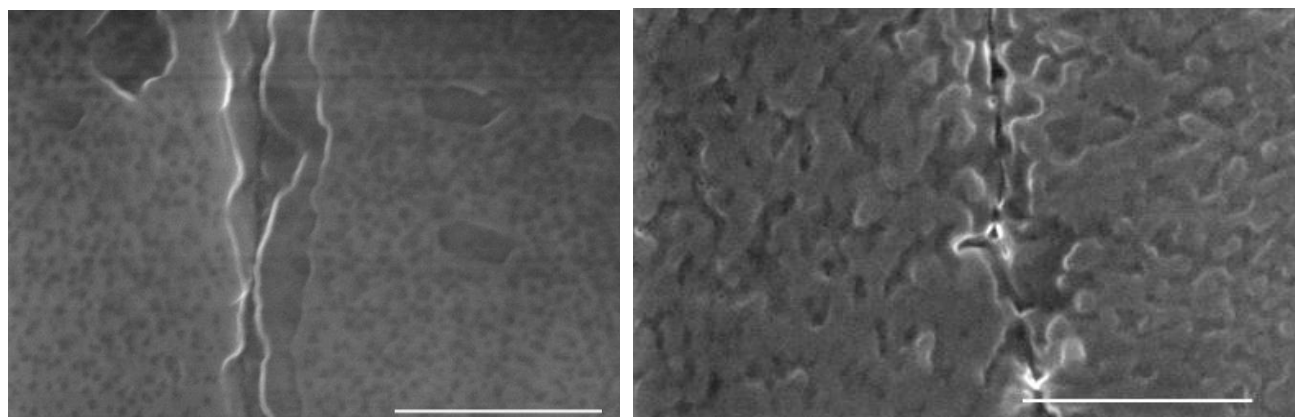


Figure 2 Two SEM images taken at the edges of tablets before and after plasma etching at different magnifications (bars represent $1\mu\text{m}$ and $0.5\mu\text{m}$ respectively) showing the tablet surface beneath the organic layer.

Reference:

- [1] N. Yao, A. Epstein, and A. Akey, *Journal of Material Research* **2006**, *21*(8), 1939-1946.
- [2] S. Blank et al. *Journal of Microscopy* **2003**, *212* (3), 280-291.
- [3] J.H.E. Cartwright and A.G. Checa. *J. R. Soc. Interface* **2007**, *4*, 491-504.
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