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After acquiring the nanoindenter (Hysitron Triboindenter TI-950), we have been largely successful in obtaining high quality, high-resolution mechanical (i.e., modulus and hardness) maps of multiple biological composites. This includes the mechanical properties of the nacreous region from the California red abalone, the hard and luminescing shell (Hinea brasiliana, in collaboration with Dr. Dimitri Deheyn), the ultrahard and abrasion resistant teeth from the giant mollusk, Cryptochiton stelleri, and the dactyl club from the stomatopod Odontodactylus scyllarus.

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Final Report (2011)

Procurement of a Nanoindenter for Structure-Function Analyses of Biologically Inspired High Performance Composite Materials

PI: David Kisailus, UC Riverside

Agency: Air Force Office of Scientific Research

Program Manager: Dr. Hugh DeLong, Mathematics, Information and Life Sciences Directorate

Abstract

After acquiring the nanoindenter (Hysitron Triboindenter TI-950), we have been largely successful in obtaining high quality, high-resolution mechanical (i.e., modulus and hardness) maps of multiple biological composites. This includes the mechanical properties of the nacreous region from the California red abalone, the hard and luminescing shell (*Hinea brasiliana*, in collaboration with Dr. Dimitri Deheyn), the ultrahard and abrasion resistant teeth from the giant mollusk, *Cryptochiton stelleri*, and the dactyl club from the stomatopod *Odontodactylus scyllarus*.

The nanoindenter has enabled us to make significant contributions in uncovering details about the ultrastructural – mechanical relationships of the various regions within these biological composites and has allowed us to derive new design strategies for the synthesis of impact and abrasion-resistant composites.

Through the acquisition of this nanoindenter, we have also enabled the training and education of post-doctoral researchers, graduate and undergraduate students. Personnel that have utilized this instrument include: Dr. James Weaver (post-doctoral researcher), Mr. Garrett Milliron (Ph.D. student), Mr. Christopher Salinas (Ph.D. student, Hispanic minority), Ms. Qianqian Wang (Ph.D. student), Mr. Steven Herrera (undergraduate student, Hispanic minority) and Mr. Brian Weden (undergraduate student). In addition to training and education, this equipment has enabled our lab to collaborate with multiple PIs around the world, including: Dr. Elaine DiMasi (Brookhaven National Lab), Dr. Pablo Zavattieri (Purdue University), Dr. Ali Miserez (Nanyang University), Dr. Dimitri Deheyn (Scripps, UCSD), Dr. Masa Rao (UCR).

Finally, through the procurement of this instrument, the data we have acquired data that has lead to outreach events at the Riverside Metropolitan Museum (June, 2011), the San Diego Zoo (September, 2011) and the Southern California Conference for Undergraduate Research (November, 2011). During these events, as many as 11 of my 14 undergraduates working in the Biomimetics and Nanostructured Materials Lab have presented their research to a public audience.

Research objectives relevant to DoD

The proposed instrumentation has greatly enhanced the quality of research and research-related education currently funded by the DoD as well as established new research capabilities at the

University of California, Riverside, for performing research potentially of interest to the DoD.

AFOSR's mission is to manage the discovery and initial development of leading-edge research while identifying potential new concepts and opportunities that will serve the Air Force in the future. The basic research is focused primarily on maintaining a critical scientific foundation that facilitates long-term technical opportunities. This instrument has helped research encompassing three research areas within the Aerospace, Chemical and Material Sciences Directorate: Mechanics of Multifunctional Materials and Microsystems, Polymer Matrix Composites, and Structural Mechanics programs. The research at UCR bridges the priorities of this Directorate with those of the Mathematics, Information and Life Sciences Directorate, which has supported the **PI's current research (Biologically Inspired Synthesis and Structure-Function Analysis of High Performance Composites, award #FA9550-09-1-0376, Program Manager: Dr. Hugh DeLong)**.

The Mechanics of Multifunctional Materials and Microsystems program main goals are to establish safer, more durable aerospace vehicles and platforms with improved performance characteristics; and to bridge the gap between the viewpoints from materials science on one side and structural engineering on the other in forming a science base for the materials development and integration criteria. The Polymer Matrix Composites program current research interests include nanocomposite concepts that are relevant to improving or replacing current carbon fiber reinforced composites or incorporating multifunctionalities in the laminate structures. The research targets in this area can address the matrix resin, fiber, ply or laminate level. Finally, the Structural Mechanics Program encourages fundamental basic research that will generate understanding, models, analytical tools, numerical codes, and predictive methodologies validated by carefully conducted experiments.

In addition, our research that involved the use of this instrumentation also falls under the Mathematics, Information and Life Sciences Directorate because much of the inspiration for our projects is guided by natural systems. Thus, we focused on the Natural Materials and Systems Program. Our proposed research touched all three of these program objectives by (1) bridging and integrating materials science and mechanics, (2) investigating polymer (polypeptide / polysaccharide) matrix composites with laminate features, and (3) developing a set or system of analytical tools for the understanding of structure-function relationships in composites. We established structure-function relationships in mineralized and biologically inspired composite materials by overlaying ultrastructure, chemical and mechanical maps of regional features expanded on a global scale. From these combined maps, we interrelated these observations to identify dominant mechanisms at relevant scales and extract design strategies for mimetic syntheses.

In order to address the above AFOSR needs, the PI, a recent tenure-track hire at University of California, Riverside (UCR), Bourns College of Engineering, initiated several projects that investigate structure-function relationships of high-performance composites as well as developed synthetic strategies towards biologically inspired composites.

One major focus area of the Kisailus lab at UCR is to develop new structural materials with high strength and durability, light weight, and damage tolerance. Biomineralized tissues are used as model systems for the understanding of structure-function relationships that serve as templates for biologically inspired systems. These biological systems demonstrate the ability to control nano- and microstructural features that significantly improve mechanical performance of otherwise brittle materials. By investigating the structure-function relationships of these mineralized structures using modern chemical, morphological, and mechanical characterization techniques, we will develop the necessary synthetic tools for the design and fabrication of light-weight, ultrahard and tough composites that mimic the various design elements and performance properties present in the biological systems.

Much of our work relies the elucidation of the primary toughening mechanisms of these unique composite materials through the following investigations:

1. A detailed, three-dimensional map of the nano- and microstructural features, with specific mineral and organic composition, morphological and phase information.
2. A complementary mechanical investigation of the regional structures.
3. Bio-mimetic synthesis experiments to understand organic-inorganic interactions that control mineral composition and phase in order to develop large-scale composite materials.

The acquisition of the nanoindenter has enabled us to significantly enhance our research capabilities towards all of these investigations by uncovering key elements in different composites that provide them with such remarkable performance.

Accomplishments based on acquisition of the Nanoindenter:

The following are overviews of results that have been attained based on acquisition of the nanoindenter:

Numerous ongoing research projects in the Kisailus lab are investigating structure-function relationships in a wide range of self-sharpening, abrasion-resistant, and impact tolerant biological structures.

Four of the current major research projects that would significantly benefit from this set of instruments focus on investigating structure-function relationships in three distinct types of impact tolerant biological composites; the microlaminate nacreous layer of mollusk shells and the dactyl clubs of stomatopod crustaceans and the ultrahard, mineralized teeth in Chitons. The fourth project, to be performed in collaboration with Professor Masa Rao at UCR, would investigate micro-and nano-mechanical properties of metallic micro-electrical-mechanical systems (MEMS).

Initiated through the analysis of biomineralized composite materials, the first three projects focus on the systematic study of nano- and micro-structural features that afford these biomineralized tissues enhanced fracture toughness. Based on the results obtained from these studies, bio-mimetic / inspired tools will be developed and demonstrated for the design and fabrication of ultra-hard, fracture resistant materials.

Project 1: AFOSR funded "Biologically Inspired Synthesis and Structure-Function Analysis of High Performance Composites"

The goal of this project is to elucidate the toughening mechanisms of nacre, an organic-inorganic composite found in the inner layer of many mollusk shells (Figure 1) and to apply the lessons learned from these studies toward the fabrication of synthetic high-performance composites.

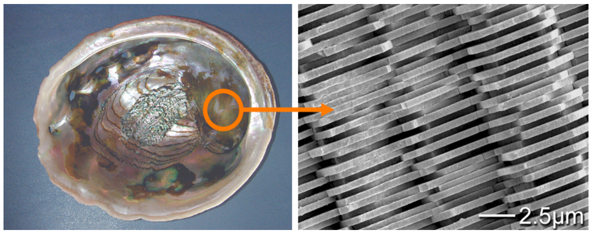


Figure 1: Cross-sectional electron micrograph of nacre that depicts the hierarchical assembly of aragonitic tablets. The assembly of nano- and microstructured tablets encased within an organic matrix afford significant enhancement of its mechanical properties.

A major component of this research will be the development of specific techniques for the fabrication of three-dimensional scaffolds of controlled geometries that replicate the features found in the nacreous organic matrix and more specifically, to identify the requisite micro- and nano-scale morphological features that may contribute to the bulk mechanical properties of nacre (Figure 2). One approach through which this will be accomplished is through the use of fused deposition modeling (FDM), a type of rapid prototyping or rapid manufacturing (RP) technology commonly used for the synthesis of engineering materials.

The PI and his collaborator, Dr. Pablo Zavattieri, have initiated this work through AFOSR (Program Manager: Hugh DeLong, Deputy Director, Mathematics, Information and Life Sciences Directorate) for the development of ultra-hard impact resistant composites. The involvement of one of the world's largest manufacturing companies provides a pathway to eventual commercialization of the technologies in products of value to the Air Force.

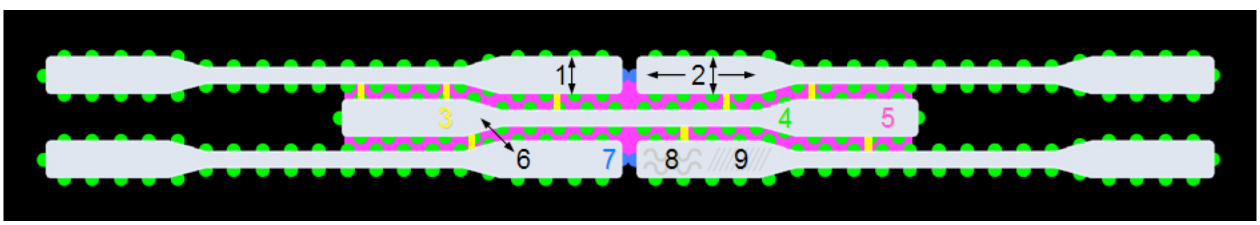
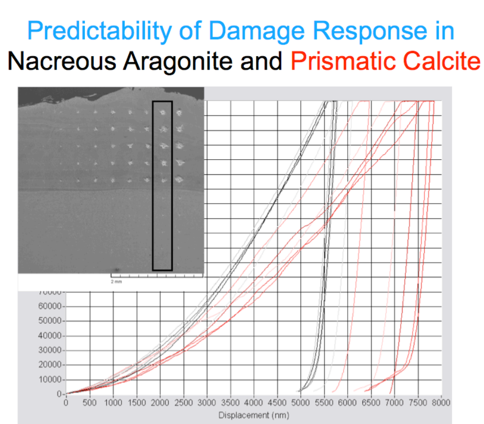


Figure 2: Micro- and nano-scale morphological features that may contribute to the bulk mechanical properties of nacre: (1) tablet thickness, (2) tablet aspect ratio, (3) mineral bridges (vertical tabular interconnects), (4) nano-asperities, (5) thickness and composition of the organic matrix, (6) degree of tablet overlap, (7) lateral tablet interconnections, (8) tablet waviness, (9) tablet mineral composition and crystallinity. The relative contributions of each of these features are being investigated via rapid prototyping using fused deposition modeling.



As part of this work, we have evaluated mechanical performance of the Calcitic and Aragonitic (nacreous) regions of the abalone shell (Figures 3, 4). Here, we can see that the damage is significantly mitigated in the nacreous regions while cracks formed in the Calcitic region propagate through the material.

Figure 3. Nanoindentation of cross section of abalone shell. Insert is nanoindentation map of Calcitic region (upper) and aragonitic region (lower).

Identifying the crack propagation mechanisms helps to identify new designs for impact resistant materials, so the nanoindentation work done with the new TI-950 was critical.

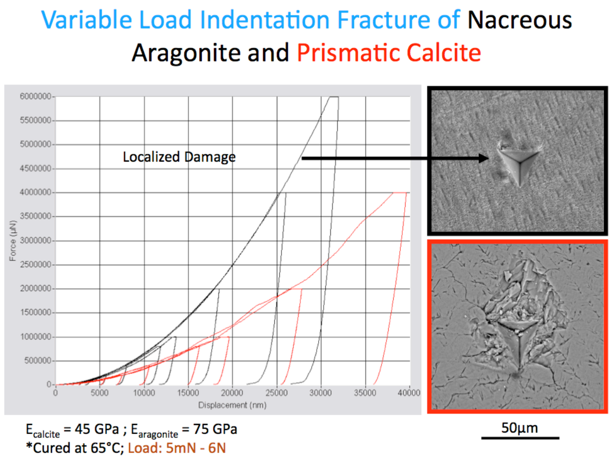


Figure 4. Nanoindentation of cross section of abalone shell. Insert is nanoindentation map of Calcitic region (lower) and aragonitic region (upper).

Project 2: NSF-funded "Structure-Function Analysis of an Ultra-hard Biological Composite"

The goal of this project was to investigate the hyper-mineralized combative dactyl club of the stomatopods (Figure 5), a group of highly aggressive marine crustaceans. This ultrahard organic-inorganic composite structure is capable of inflicting significant damage following impact with a wide variety of biomineralized structures (e.g., mollusk shells, crab exoskeletons, the skulls of small fish, and the occasional weary fisherman).

Figure 5: Dactyl modifications in stomatopods that that either hunt by impaling their prey with spear-like structures (left) or those that smash them with a powerful blow from a heavily mineralized club (right) stomatopods. (Illustrations adapted from Brooks, 1886). Species: *Neoanchisquilla sp.* (left) and *Odontodactylus scyllarus* (right).

In fact, these formidable structures are capable of accelerations to 10,400 g and speeds of 23 m/s from a standing start (Patek, et al., 2004). Because of their rapid strike, they can generate cavitation bubbles between the appendage and the striking surface. The collapse of these cavitation bubbles produces significant forces on their prey in addition to the instantaneous forces of 1,500 N that are caused by the direct impact of the dactyl club (Patek and Caldwell, 2005). Despite these significant forces, the dactyl clubs are extremely fracture-resistant and are able to tolerate thousands of highly energetic blows, a characteristic that can be directly linked to their ultrastructural features. This research model is quite different form that of nacre due to its multi-phasic architecture and in the fact that it performs primarily an offensive, rather than a defensive function. As with the nacre research, the ultimate goal of this project was to not only understand the structure-function relationship us this unique impact tolerant and abrasion resistant biological structure, but to ultimately develop synthetic engineering analogs that exhibit equally impressive mechanical properties.

Combined mechanical characterization experimental techniques using depth-sensing nanoindentation have been used to characterize the modulus and hardness of cross-sections of the dactyl clubs.

We have acquired a new nanoindentation system that is state of the art. This Hysitron TI-950 system was used to perform depth-sensing nanoindentation experiments on the polished longitudinal and cross-sectional specimens of the dactyl clubs to create the multi-sectional modulus maps and line scans. Multiple indentations (at 1mN) were performed at different locations (from the impact surface to the club interior) on the dactyl club to obtain the depth and region dependent mechanical properties. Figure 6 shows a nanoindentation map (modulus) of the cross section of the dactyl club.

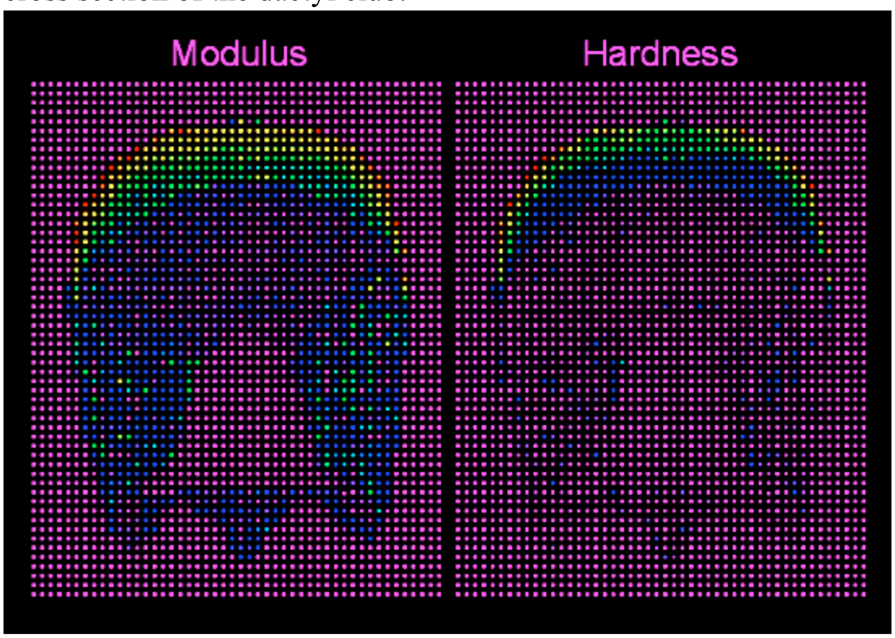


Figure 6. Nanoindentation map depicting the elastic modulus and hardness of regions within the dactyl club. The modulus was highest in the exocuticle, reaching up to 80 GPa, while the less mineralized endocuticle had a modulus of 5 GPa. Similarly, the hardness ranged from ca. 3.5 GPa in the exocuticle to ca. 0.8 GPa in the endocuticle. The purple regions surrounding the club are epoxy-based.

The regions within the club display different mechanical properties. Note the large differences in modulus across two interfaces (i.e., 5 GPa – 30 GPa – 65 GPa), similar to what is observed in a human tooth from dentin – dentin/enamel junction – enamel.

It is clear that higher resolution scans are necessary to interrogate local structure-mechanical property relationships. Thus, we acquired high-resolution nanoindentation scans (Figure 7) that not only show the difference in modulus from the exocuticle to endocuticle, but also display a periodicity within the endocuticle.

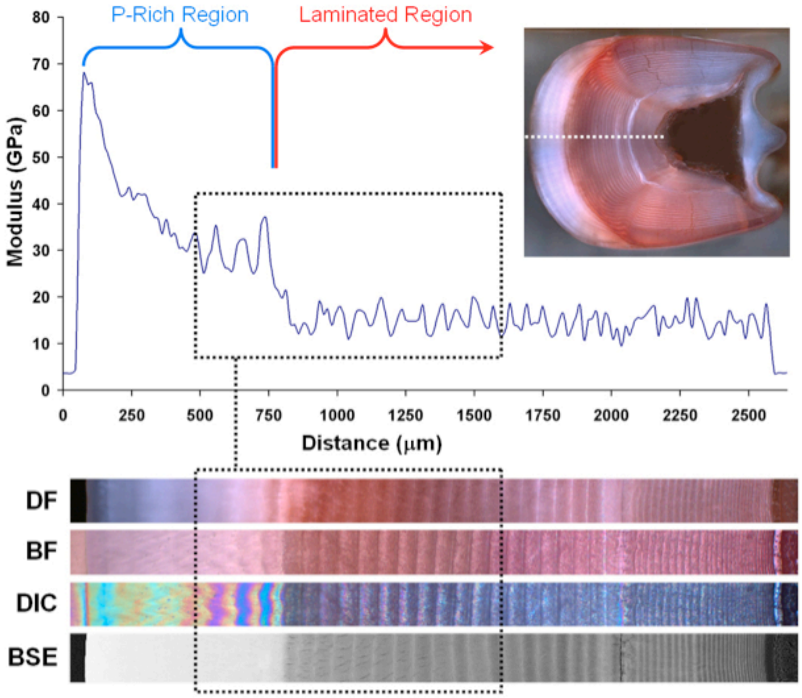


Figure 7. (Top) Nanoindentation line scan of elastic modulus from exocuticle inward to the endocuticle. (Lower) Optical microscopy uncovering the graded nature of the endocuticle region.

The higher resolution linescan reveals that the endocuticle is a functionally graded composite with regard to modulus. These structures are known to have excellent fracture mitigation properties as evidenced from the charge contrast images.

Project 3: "<u>Structure-function relationships in the radular teeth of Chiton</u>"

The chitons (Mollusca, Polyplacophora) are an ancient group of mollusks with a fossil record dating back nearly half a billion years. Despite their long and successful history and their ecological importance in rocky coastal habitats they are a comparatively small group with about 650 modern species. Chitons are flattened and usually elongated mollusks that are protected dorsally by a shell consisting of eight overlapping plates. The foot is broad and powerful, well adapted for clinging tightly to the hard surfaces on which the animal grazes for algae. Like most other groups of mollusks, the chitons have a radula, a rasping, toothed conveyor belt-like structure, which is used for feeding. The composition and morphology of the radular teeth vary from group to group and depend to a large extent on the dietary specifics and the mechanical properties of the substrates on which they feed.

Nanomechanical analyses of polished cross-sections through both the tooth tip and mid-region reveal that the two mineral phases (the magnetite veneer and the core of weakly crystalline hydrated iron phosphate) exhibit distinct mechanical properties (Figure 8). The magnetite veneer has a modulus ranging from 90 to 125 GPa and a corresponding hardness ranging from 9 to 12 GPa. To the best of our knowledge, these values represent the highest modulus yet reported for a biomineral. The hardness is notably about 3 times higher than that of enamel and nacre, which exhibit indentation hardness and modulus of 3 - 4 GPa and 65 – 75 Gpa, respectively, making this material exceptionally well suited for the continuous scraping activity of the radular teeth. In contrast, the weakly crystalline core region has a modulus of ca. 25 GPa. Mechanical mapping of cross-sections through these two regions of the teeth reveals a distinct gradient in mechanical properties with the modulus of the leading edge of the tooth ca. 15% higher than that on the trailing edge. This design strategy results in an uneven wear pattern along the scrapping edge of the tooth and establishes a self-sharpening condition, an observation consistent with radula structural studies on other species.

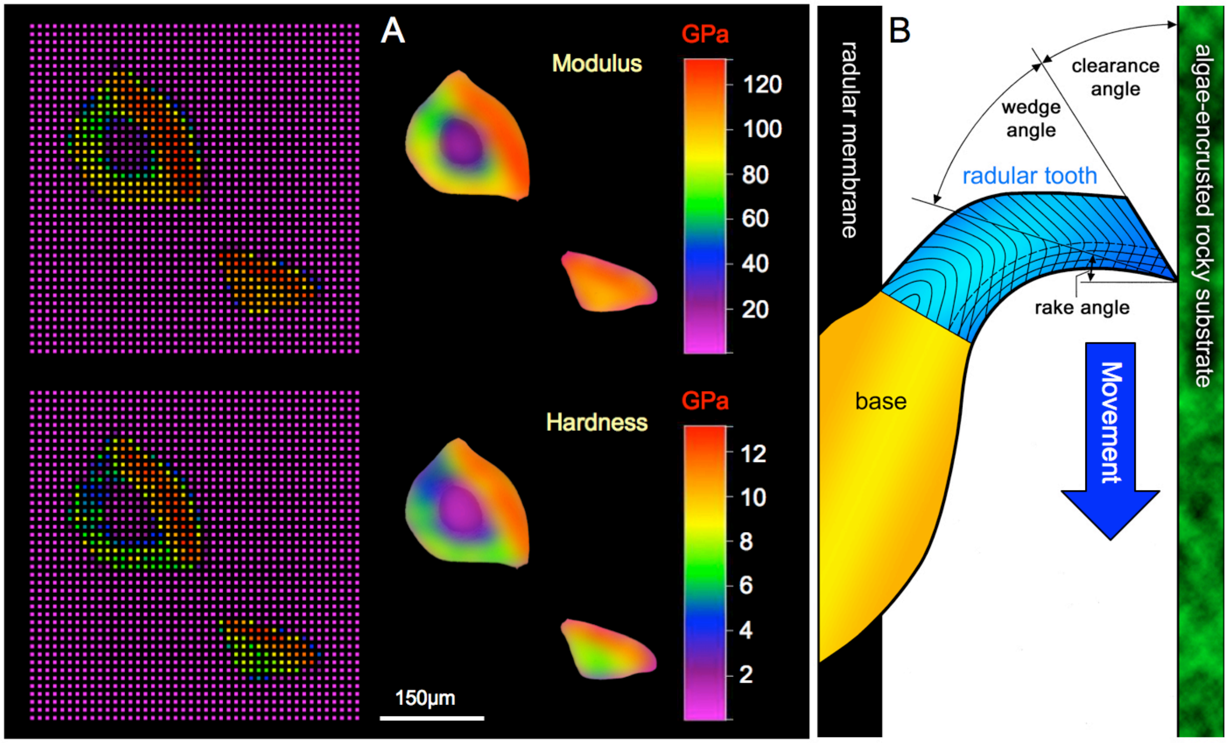


Figure 8: Nanomechanical testing of radular tooth cross-sections from *C. stelleri*. (A) Indentation (left) and the corresponding gradient (right) maps of modulus (upper) and hardness (lower) through a tooth tip and mid-region reveal that the leading edge of the tooth has a higher modulus and hardness than the trailing edge, thus establishing the self-sharpening condition illustrated in (B). The direction of tooth movement against the substrate is indicated by the blue arrow.

Project 4: "Robust MEMS Materials for Enhanced Survivability (collaborator: M.P. Rao)"

Traditionally, materials selection has been limited in MEMS applications, due primarily to the predominance of microfabrication processes and infrastructure dedicated to silicon. While silicon has proven to be an excellent material for many applications, no one material can meet the needs of all applications. This is particularly evident in military systems where silicon's intrinsic brittleness limits survivability in high-G shock environments. Survivability can be enhanced through robust mechanical design and packaging, but this invariably increases cost and complexity, thus illustrating the need for development of viable alternatives. This project seeks to develop advanced micromechanical materials and process technologies that address the survivability issue at its root. Specifically, the ultimate goal is to enhance the fundamental survivability of the materials used for micromechanical devices via enhancement of their toughness using batch-scale fabrication techniques that are compatible with conventional semiconductor process methodologies. This will facilitate manufacturability by leveraging current process infrastructure and help ensure reduced cost by exploiting the economy of scale inherent to high-volume batch-fabrication.

Bulk Titanium MEMS

The intrinsic brittleness of silicon provides the impetus for development of more robust alternatives. Metals show distinct promise in this regard due to their high fracture toughness. One metal of particular interest is titanium, due to its high strength to weight, excellent corrosion resistance, and superior fatigue properties. However, process technology that enables fabrication of complex, high-aspect-ratio micromechanical structures in titanium was, until recently, unavailable. A short time ago we reported the development of micromachining techniques that enable, *for the first time*, anisotropic deep reactive ion etching of bulk titanium substrates. As demonstrated in Figure 9, this technology provides the opportunity for fabrication of titanium-based devices with a degree of design sophistication that would be difficult if not impossible to achieve with prevailing metal micromachining methods.

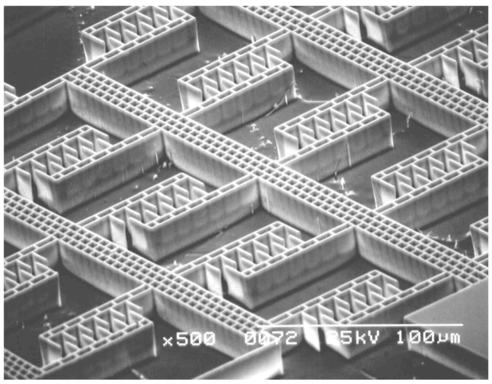


Figure 9: Scanning electron micrograph of a bulk micromachined titanium comb drive. Etch depth is 20 μm and minimum feature size is 1 μm.

In this work, nanomechanical testing (using the Hysitron Nanoindenter) was performed on titanium posts (Figure 10) to determine their strength as a function of pillar thickness. These posts were being tested to determine their mechanical viability in medical stents.

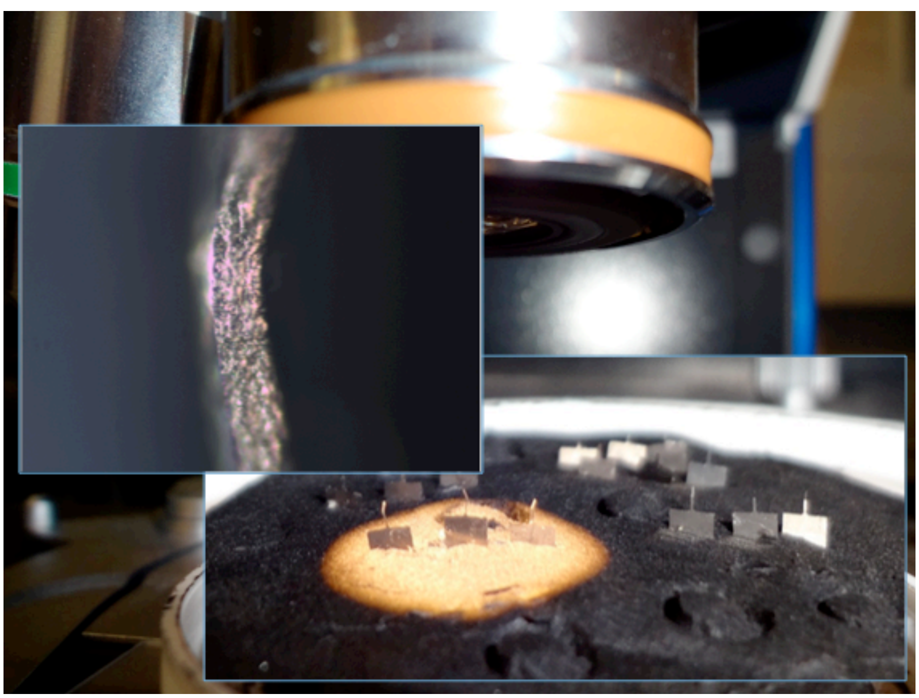


Figure 10. Nanomechanical testing of titanium posts to be used in medical stents.

Supported Personnel and Collaborations:
<u>Training, Education, and Outreach Achievements</u>

Besides providing scientific knowledge on multiple projects, acquisition of the nanoindenter has enabled training, education, and outreach.

Through the acquisition of this nanoindenter, we have also enabled the training and education of post-doctoral researchers, graduate and undergraduate students. Personnel that have utilized this instrument include: Dr. James Weaver (post-doctoral researcher), Mr. Garrett Milliron (Ph.D. student), Mr. Christopher Salinas (Ph.D. student, Hispanic minority), Ms. Qianqian Wang (Ph.D. student), Mr. Steven Herrera (undergraduate student, Hispanic minority) and Mr. Brian Weden (undergraduate student). In addition to training and education, this equipment has enabled our lab to collaborate with multiple PIs around the world, including: Dr. Elaine DiMasi (Brookhaven National Lab), Dr. Pablo Zavattieri (Purdue University), Dr. Ali Miserez (Nanyang University), Dr. Dimitri Deheyn (Scripps, UCSD), Dr. Masa Rao (UCR).

Finally, through the procurement of this instrument, the data we have acquired data that has lead to outreach events at the Riverside Metropolitan Museum (June, 2011), the San Diego Zoo (September, 2011) and the Southern California Conference for Undergraduate Research (November, 2011). During these events, as many as 11 of my 14 undergraduates working in the Biomimetics and Nanostructured Materials Lab have presented their research to a public audience.

The program for this event is shown below:

Publications:
Two publications have resulted since the acquisition of this equipment and two additional manuscripts are in preparation.

Interactions/Transitions:
We have established relationships with General Motors and MVP RV (a small RV company in the Inland Empire of Southern California interested in making light-weight electric vehicles.

Conclusions: The acquisition of this system has not only greatly enhanced our capability to carry out research activities related to composite structure-function, but has also benefited the PI's and other researchers' overall capabilities in materials research. By understanding structure-function relationships and developing synthesis strategies to biomimetic composite materials, which have proved to be important for DoD applications, we have aligned our research activities with multiple DoD missions.