FINAL REPORT
NASA GRANT #- NAG1-01-003

Project Title: Biomimetic, Self-Healing Nanocomposites for Aerospace Applications

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Project Period: 10/1/00-9/30/03

I. Summary of Most Significant Findings:

A. Lustrin-mimetic Self-Healing Polymer Networks:

This aspect of our work focused on the structure, function, and biomimetic replication of the structure and function of "lustrin", the novel self-healing elastomeric adhesive (multi-functional) protein polymer we discovered in the abalone shell. Our previous work (involving gene cloning and sequencing, protein purification and characterization, and single molecule pulling experiments (using the atomic force microscope as a single molecule strain-gauge) revealed that lustrin is a modular, repetitive polymer containing numerous sacrifical bonds (intermediate -strength cross-links, that reversibly rupture at an applied stress just less than that required to break the polymer backbone. The capacity of this material to absorb energy is greatly enhanced by the "hidden length' that is opened following the rupture of these sacrifical bonds. Furthermore, the sacrificial bonds stochastically reform, in a process driven by the entropically driven refolding of the polymer. In work completed in this project, we have demonstrated that these fundamental principles underly the energy-diseprsive and self-healing performance of a wide range of biological high-perfromance composites, and that they can be translated to form synthetic composites with comparable performance.

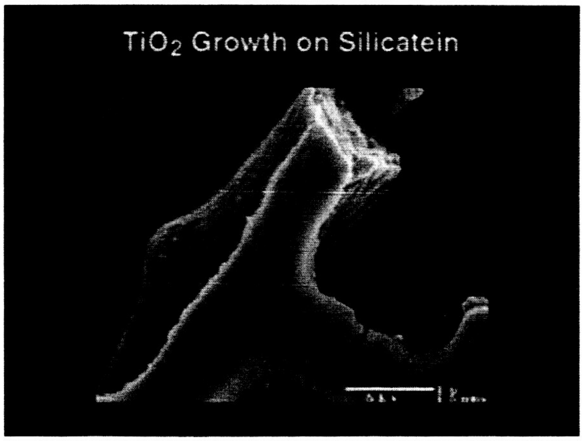
In collaboration with Prof. John Evans (who spent a sabbatical year with Prof. Morse at UCSB) and Evans' lab at NYU, we have been using liquid NMR and molecular modeling to analyze the structural basis for the mechanical performance of lustrin (see publications). Then in collaboration with Profs. Galen Stucky and Paul Hansma and postdoctoral Dr. John Harreld, we translated these principles to make self-healing, energy-dispersive elastomeric adhesives. To achieve the properties of lustrin in a synthetic material, we have synthesized silsesquioxane-peptide hybrid materials, in which lengths of polydimethylsiloxane are cross-linked by peptide strands containing reversible non-covalent "sacrificial" bonds. A wide variety of potential sacrifical bonds (ionic, H-bonds, van der Waals, hydrophobic, and cation-pi-electron) is under investigation. Synthetic challenges thus far encountered include principally the limitation on molecular weight; analytical challenges include characterization of the synthesized bulk materials.

In collaboration with Prof. Paul Hansma and his team at UCSB, we also have discovered related self-healing properties in other biological composites such as bone, and in other biopolymers such as collagen.

This work subsequently formed the basis for continuation via a multi-investigator, multi-institutional NASA-supported URETI program focused on Bio-Inspired Routes to Multifunctional Materials.

B. Nanostructure-directing Catalysis of Synthesis of Electronically and Optoelectronically Active Metallo-oxanes and Organometallics:

Using "silicatein", the structure-directing polymerization catalyst that we discovered occluded in the biosilica structures made by sponges, and biomimetic analogs of silicatein that we have developed based on our genetic dissection of the mechanism of action of the silicatein, we have now extended this work to make nanostructure-directed titanium dioxide, gallium oxide, zinc oxide, and polymers of optoelectronically active organometallics. In each of these cases, polycondensation of the appropriate metal oxide or organometallic siloxane precursor resulted in polycondensation of the covalent network product using the silicatein protein filaments as both catalyst and template. The organometallic we polymerized exhibits a color change upon reversibly binding sulfur dioxide, suggesting potential usefulness both as a sensor and as a chemically controlled optoelectronic switch. The goal of our work continued in this project has been to harness the biological mechanisms discovered in silicatein to help us make multi-functional and lighter weight materials for aerospace applications. This approach also subsequently formed the basis for continuation via the multi-investigator, multi-institutional NASA-supported URETI program focused on Bio-Inspired Routes to Multifunctional Materials described above.

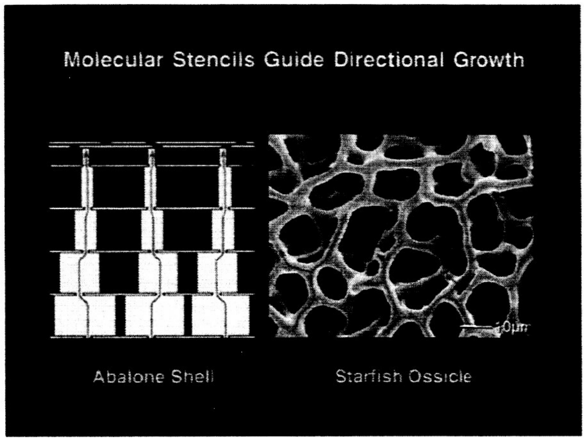


TiO2 polycondensation is catalyzed and templated on the surface of the underlying filament of silicatein, resulting in structure-directed growth of the mineral.

These reactions are catalyzed at low temperature (20 °C) and neutral pH.

C. New Discovery that Molecular Stencils Control Directional Growth to Form Light-Weight Mineral Foams:

In our enabling work upon which this project was based, we also discovered several unanticipated mechanisms that contribute to the control of the nanostructure and properties of the high-performance microlaminate of the abalone (molluscan) shell. We now have made the surprising discovery that the mechanism of "molecular stenciling" responsible for the hierarchical organization and macrostructure of this shell (below, left) also is apparently responsible - with an interesting "twist" for the light-weight mineral foam that provides the protective skeletal elements in starfish and sea urchins. In these species, calcium carbonate skeletal elements are synthesized in a remarkable, highly porous "foam", combining mechanical robustness with light weight (below, right). Our X-ray diffraction analyses demonstrate that this material is unicrystalline, suggesting that it is synthesized by a manner closely similar to that controlling the microlaminate of the shell: directional growth of the calcium carbonate from a single plane of nucleation through the tortuous interstices between bundles of collagen fibrils apparently guides the growth of the interconnected network of completely coherent crystalline material to produce the foam-like structure. We are exploring the use of this strategy for the synthesis of coherent metal and crystalline foams for energy storage functions in light-weight multi-functional materials.


Molecular Stencils Guide Directional Growth

(left:) Our previous work showed that nanopores in fenestrated sheets of protein (green) act as molecular stenils, guiding the growth of crystals of CaCO3 from one layer to the next in abalone shell.

(right:) We now have found that the tortuous interstices between bundles of collagen fibers similarly act as molecular stencils, guiding the directional growth of CaCO3 from a nucleating surface to form the light-weight "foam" of armor in the starfish and sea urchin skeleton.

II. **Publications**:

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III. Patents:

Modular Energy-Dispersing Material and Methods For Using It U.S. Patent No. 6,376,636 B1. . Issued 4/23/02.

Self-Healing Organosiloxane Materials Containing Reversible and Energy-Dispersive Cross-Linking Agents. US # 10/193,533; Pending.

Methods, Compositions and Biomimetic Catalysts for In Vitro Synthesis of Silica, Polysilsesquioxanes and Polymetallo-Oxanes. Patent No. 6,670,438; Issued Dec. 30, 2003.

Structure-Directing Synthesis of Metal Oxides and Nitrides, Metalloid Oxides and Nitrides, Rare-Earth Oxides and Nitrides for Electronic and Other Applications. UC # 2002-524; Pending.

Bifunctional Catalysts and Methods for Use for Synthesis of Impermeable Coatings, Membranes, Sealants Encapsulants, Insulators, Polymers and Materials of Silica, Glass, Silicones and Polymetallo-Oxanes at Low Temperatures and Neutral pH. US Provisional Application filed April 4, 2001; converted to Full US patent application; pending; PCT Report accepted all claims