Mesocrystalline Ordering and Phase Transformation of Iron Oxide Biominerals in the Ultrahard Teeth of Chitons

Wang T[1], Montroni D[1,2], Nemoto M[3], Kisailus D[1]*.
*lead presenter: david.k@uci.edu
1 University of California at Irvine, USA
2 University of Bologna, Italy
3 Okayama University, Japan

Natural systems have evolved efficient strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials.

In this work, we investigate an organism that have taken advantage of hundreds of millions of years of evolutionary changes to derive structures, which are not only strong and tough, but also demonstrate abrasion resistance. All of this is controlled by the underlying organic-inorganic components. Specifically, we discuss the formation of heavily crystallized radular teeth the chitons [1-3], a group of elongated mollusks that graze on hard substrates for algae. Here, we reveal the biologically-controlled structural development of the hard, outer magnetite-containing shell of the chitin teeth. Specifically, we identify the formation of a series of mesocrystalline iron oxide phases, templated by chitin-binding proteins [4-6]. The initial domains, consisting of ferrihydrite mesocrystals with a spherulite-like morphology, undergo a solid-state phase transformation to form magnetite while maintaining mesocrystallinity, likely via a shear-induced solid-state reaction, without any noticeable architectural changes. Subsequent growth via Ostwald ripening leads to nearly single crystalline rod-like elements. In addition, we identified an interpenetrating organic matrix that, at early stages of tooth development, potentially contains iron-binding proteins that guide the self-assembly of the mesocrystalline mineral and influence the preferred orientation of the later-formed magnetite nanorods, which ultimately determines the mechanical behavior of the mature chiton teeth.

From the investigation of synthesis-structure-property relationships in these unique organisms, we are now developing and fabricating multifunctional engineering materials for energy conversion and storage.

References

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