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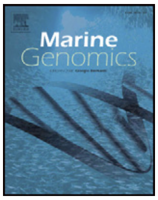
Cells to Shells



Biomimetic and bio-inspired uses of mollusc shells

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ABSTRACT

Climate change and ocean acidification are likely to have a profound effect on marine molluscs, which are of great ecological and economic importance. One process particularly sensitive to climate change is the formation of biominerals in mollusc shells. Fundamental research is broadening our understanding of the biomineralization process, as well as providing more informed predictions on the effects of climate change on marine molluscs. Such studies are important in their own right, but their value also extends to applied sciences. Biominerals, organic/inorganic hybrid materials with many remarkable physical and chemical properties, have been studied for decades, and the possibilities for future improved use of such materials for society are widely recognised. This article highlights the potential use of our understanding of the shell biomineralization process in novel bio-inspired and biomimetic applications. It also highlights the potential for the valorisation of shells produced as a by-product of the aquaculture industry. Studying shells and the formation of biominerals will inspire novel functional hybrid materials. It may also provide sustainable, ecologically- and economically-viable solutions to some of the problems created by current human resource exploitation.

General definitions

Bio-inspired materials synthesis Concepts derived from natural processes such as biomineralization using artificial materials (Lobmann, 2007)

Biomimicry (Biomimetic) Sustainably orientated methods mimicking living organisms and ecosystems in terms of shape, material, or organisation by using living organisms or materials of a biological origin (adapted from Lobmann, 2007).

Calcination Changing a substance's physical or chemical constitution by heating in oxygen or air, but below melting or fusion points. For instance; $CaCO_3 \rightarrow CaO + CO_2$ at ~850–~1200 °C

Circular economy As opposed to a linear economy (make, use, dispose), a circular economy aims to minimise waste and pollution through improving longevity, repair, reuse, remanufacture, and recycling.

Valorisation To assign or give value to something, where value can be economic, environmental, and/or social.

Mollusc shell microstructures

Composite prismatic A variety of prismatic structures with large horizontal prisms each composed of compound prisms radiating in three directions

Crossed-lamellar Lath-like crystals arranged in "plywood" structure. The most common structure in mollusc shells (90% of gastropods and 60% of bivalves)

Foliated structure An arrangement of thin folia or sheets of calcite which intersect growth surface at a low angle (4–7°), including regularly foliated, and crossed foliated, complex crossed foliated and calcitic crossed bladed structures.

Homogeneous Granular crystals with no typical crystal form

Nacreous Tablet-like crystals arranged into columns or in sheets. The toughest layer in mollusc shells

Simple prismatic Consists of column-shaped crystals. Individual prisms arranged perpendicular to the shell surface

Biomimetic and bio-inspired technologies. Materials inspired from mollusc shell composition/structure

Additive manufacturing Layers of diverse materials built up to form three-dimensional structures. A variety of materials from polymers to metals, to ceramics can be used.

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Freeze casting Templating of porous structures into a solidified phase by the solidification of a solvent. A large variety of materials can be processed by this method, independent of the materials property.

Langmuir mono-layers, self-assembled mono-layers Surface of well-defined chemistry used for patterning crystal location and examining the influence of organics on crystal orientation and crystal phase

Layer-by-layer assembly, electrophoretic deposition Both techniques are used for fabricating functional thin films with a layered structure, one by alternately immersing a clean substrate into several solutions, other under the influence of an electric field, where a coagulation of particles turns to a dense mass.

1. Introduction

The strength, hardness, and toughness of shells produced by molluscs are major characteristics of this group that have been recognised deep into human history. The mechanical attributes of their shells, alongside their beauty and intricacy, have made the molluscs that craft them a charismatic marine group. Shells have played an important role in many aspects of human culture: they have been used widely as cutting and weight bearing tools (Douka and Spinapolice, 2012), as well as being traded for goods globally until the 20th Century (Johnson, 1970). A myriad of other historical uses could be listed. The influence of molluscs on our society and economy is not purely historical. On the contrary, society has more to gain from the study and application of molluscs and their shells. For instance, despite concerted efforts, man-made ceramics and composites, usually produced at high temperatures and/or high pressure (Tam et al., 2009), remain inferior to mollusc shells in strength and toughness (Sellinger et al., 1998; Munch et al., 2008). The hierarchy of structural features and organic/mineral phase interactions observed in shells have yet to be recreated completely (Espinoza et al., 2009). There is a growing understanding of the need to improve the sustainability of all processes. This has led some to take another look at shells to determine whether established and novel biomimetic and bio-inspired applications can be implemented and/or commercialised. Further, as aquaculture continues to expand its share of global food production (FAO, 2014), the issue of shell waste from food production will become increasingly impactful unless shells can be revalued and repurposed.

Improving knowledge on the value of shells for novel applications, and their use as an alternative to existing resources requires a solid and fundamental scientific grounding. Mollusc shells are composed of >95–99.9% $CaCO_3$, the remainder being organic matrix (Currey, 1999; Harper, 2000). The organic matrix comprises mainly proteins, glycoproteins, chitin, and acidic polysaccharides. Important components of these organic molecules are hydrophobic, referred to as “frame-work macromolecules”, and provide a three-dimensional matrix for mineral deposition. Other soluble organic macromolecules, rich in negatively charged residues, are excellent candidates for interacting with the mineral ions (Weiner et al., 1983). These molecules are essential components in the morphological variation, spatial organisation, and the mechanical and biological properties of the biominerals produced (Addadi et al., 2006; Mann, 1988). In recent decades, the primary structure of more than 40 mollusc shell proteins has been elucidated (Marin et al., 2007), and some of the proteins that control the biomineralization process have been isolated and characterised (Arakaki et al., 2015; Weiner and Dove, 2003). However, the molecular mechanisms underlying shell formation processes remain poorly understood. Some of the research presented in this special issue of “Marine Genomics” aims at contributing to our understanding of the processes of shell production at molecular and cellular levels. For instance, several studies have probed the transcriptomes of bivalves, characterising the expression of many genes involved in the biomineralization process (Bjärnmark et al., 2016-in this issue; Vendrami et al., 2016-in this issue; Yarra et al., 2016-in this issue). Further, proteins not previously recognised as being related to the shell have been characterised in a proteomic study of the clam *Mya truncata*, suggesting that a shells function goes beyond a simple protective layer, and may also be actively involved in cell signalling processes and the immune response (Arivalagan et al., 2016-in this issue).

These studies are important not only because of the fundamental questions they pose and the novel insights they provide, but also because such insights can spark new avenues for applied sciences. An understanding of the role and differential spatial expression of genes involved in mollusc shell biomineralization may help materials scientists progress in the synthesis of shell-inspired nanostructures. Similarly, a better understanding of the proteins found locked inside the shell structure will help change our modern view of shells from aquaculture being considered a waste product. The following sections will give a brief and non-exhaustive overview of the uses for biomineralization in novel biotechnology applications, and the potential application of waste shells from the aquaculture industry.

2. Shell knowledge for bio-inspiration

Mollusc shells represent an important portion of the large family of biomaterials. With our oceans warming and acidifying at a rate that exceeds historical proxies, many calcifying organisms are being challenged for survival. By studying the process of biomineralization we gain a better understanding of how molluscs may react to contemporary climate change (Vendrami et al., 2016-in this issue), and the impact that human activity is having on these ecologically- and economically-important organisms. This knowledge is also likely to inspire novel biomimetic synthesis methods which may lead to more sustainable industrial and societal practices.

Shell producing mollusc classes have recognisable shell microstructures *e.g.* “prismatic”, “nacreous”, “foliated”, “crossed-lamellar”, “composite-prismatic”, and “homogeneous” (Carter, 1990). These different calcified layers are exquisitely controlled by macromolecules. Characterisation of the shell matrix macromolecules allows a better understanding of their functions, and further refines the biomineralization model. Applied sciences look to such research in the search for innovative sustainable solutions in the production of synthetic biomaterials. Specifically, new design strategies have been inspired from the molluscan nacreous layer, the most studied of all shell microstructures (Corni et al., 2012). Nacre, in which mineral platelets arranged in single layers are staged like brickwork with biopolymer “mortar”, has been shown to be several orders of magnitude stronger than the chemically precipitated counterpart: aragonite (Jackson et al., 1988). The complex hierarchical structure of nacre may hold the key to such strength, and may provide a model foundation for stronger future biomimetic materials. This hierarchical structure comprises ~32 nm nano-grains that create a tablet that is delimited by a fine three-dimensional network of organic material, forming 0.5–10 μm “bricks”, that ultimately form a meso-structure of layers, each approximately 0.3 mm thick (Fig. 1) (Luz and Mano, 2009; Meyers et al., 2011). Biomimetic design of materials and biomaterials inspired by the structure of nacre offers a perfect model for the development of new strong, tough, and light-weight structural materials. At laboratory scale, synthetic model matrices such as Langmuir monolayers (Donners et al., 2002) and self-assembled mono-layers (Aizenberg et al., 1999) have been successfully applied to mimic the biological control exerted by an organic matrix in creating $CaCO_3$ crystals with specific orientations that distinguish them from their inorganically produced counterparts. Organic/$CaCO_3$ hybrid materials have been developed by using molecules, such as proteins, as templates or additives (Nishimura, 2015). The principle of confinement using an organic scaffold during the mineralization process has been successfully used to control crystal formation and morphology (Kim et al., 2011). Even more sophisticated bio-inspired materials with tuneable morphologies and properties

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