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Nacre-inspired nanocomposites produced using layer-by-layer assembly: Design strategies and biomedical applications

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ABSTRACT

Biomimetics constitutes an attractive strategy for the development of new functional materials in a variety of fields. Nacre is a natural composite composed of 95% aragonite and 5% organic materials with a layered and hierarchical structure which has be shown to have high toughness and mechanical strength and resistance. As such, mimicking nacre's composition and structure can be the key for the development of new materials with increased mechanical properties and stability. This review focuses on recent developments achieved in the production of nacre-like nanocomposites using the layer-by-layer deposition technique. This technique was chosen due to its ability to create nanostructured layered structures with thickness controlled at the nanoscale level using a wide range of different materials. Several examples of nacre-inspired designs of multilayer nanocomposites are overviewed, and their possible applications are discussed, in particular in the biomedical field.

Contents

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1. Introduction

Nature has always been a source of inspiration for humanity to solve all hurdles it has faced. This continues to be the case, with biomimetics appearing as a multi-disciplinary strategy that looks upon biologic structures and processes, with the objective of creating new materials or technologies that mimic those found in the biologic world [1,2].

Currently, biomimetic approaches have been used in the biomedical area to develop materials with enhanced physical and mechanical properties, bioactivity, biofunctionalization and overall improved performance. This approach relies on the identification of problems that current materials have, research on the ways that nature has solved those issues and mimic those natural solutions as to create new better materials [1,2].

One of the key problems that current structural synthetic biomaterials possess is low mechanical performance and stability. In fact, ceramic materials are generally too brittle [3], and biodegradable polymers tend to quickly lose their mechanical strength and resistance [4]. In both cases, the result can be the premature failure of the material. One solution for both problems can pass through the development of ceramic-polymer composites. Ideally, this would result in materials with higher toughness when compared to regular ceramics, and higher mechanical strength and resistance for biodegradable polymers [5,6].

Nature has already developed a ceramic-polymer composite that shows those same desired properties [7,8]. Nacre is a layered structure that naturally appears in the shell of several molluscs composed by aragonite tiles connected by an organic matrix, and is responsible for providing the shell with increased toughening, by allowing the dissipation of mechanical energy. It is the combination of its composition and of its layered and hierarchical structure that provides nacre with its outstanding features [9,10].

Several different strategies have been proposed to develop nacre-like composites, using different processing techniques [6,10]. Among these techniques, layer-by-layer (LbL) deposition appears as one of the most appealing due to its ability to create nanostructured layered structures using a wide range of different materials, with thickness controlled at the nanoscale level [6,11,12]. This review will focus on the identification of the different structural features and properties on nacre that should be considered in the design and production of nacre-inspired nanocomposites using the LbL deposition technique. Furthermore, we overview the potential of using such materials in the biomedical field.

2. Nacre

2.1. Definition and structure

In most molluscs of the bivalve and gastropods classes, the shell is composed by three main layers: the periostractum (outer layer, composed of hardened protein), the prismatic (middle layer, composed of columnar calcite) and nacre (inner layer, composed by aragonite and organic material). While the exterior layers are brittle and hard, providing the shell with resistance to penetration from external impact, nacre provides toughening, by allowing the dissipation of the mechanical energy [9,13].

Nacre is composed of 95 wt.% of aragonite, a crystallographic form of $CaCO_3$, and 5% (wt) of organic materials, such as proteins and polysaccharides. This organic matrix plays an important role in spatial and chemical control of the crystal nucleation and growth, microstructure and toughness enhancement [9,10]. As an example, the presence of organic material in nacre provides an increase on fracture toughness up to 9 times of that of monolithic aragonite (3.3–9 MPa $m^{1/2}$ and 1 MPa $m^{1/2}$, respectively) [9,14,15].

In the broader sense, nacre is composed by a layered structure of aragonite tiles connected through an organic matrix, as shown in Fig. 1 A. Specifically, nacre is in fact composed by a hierarchy of structures that range from the nano to the macro-scale, similar to what is observed in other structural tissues [9,10,16]. Nevertheless, it is possible to distinguish two different nacre types, based on the organization of those structures. Columnar nacre, found in gastropods, has similar-sized tiles packed up concentrically, while sheet nacre, found in bivalves, consists of tiles stacked in a "brick wall" pattern. In columnar nacre, it is also important to distinguish the core areas (where tiles of the same column meet) and the overlap areas (were tiles from different columns overlap) due to the different stresses experienced on these areas [9,16].

The building blocks of nacre are polygonal aragonite nanograins that are connected by biologic polymers, forming aragonite tiles or tablets. When these tiles are put under mechanical deformation, the nanograins suffer rotation and deformation, which allows for energy dissipation. This in return provides the aragonite tiles a ductile nature that is relevant for nacre's high fracture toughness [9].

In both nacre types it is also possible to observe mineral bridges connecting different tiles. These bridges, which protrude through the organic matrix, not only allows continued mineralization on the organic layers, but also improve their mechanical properties and prevent crack extension on nacre [9].

2.2. Mechanical properties

2.2.1. Micro-mechanical properties

Due to its structure, nacre behaves differently according to the direction of the applied compressive or tensile load.

While compressive and tensile stress values vary with the different existent nacres, in a general way nacre's compressive strength is higher when exerting perpendicular loads, while its tensile strength is higher when parallel loads are applied. Compressive strengths are also generally larger than tensile strengths. These results were obtained from sample cubes with 5 mm sides, cut from nacre of red abalone shells [9,19,20]. A similar compressive behaviour could also be observed in nacre-inspired composites produced by freeze casting, on sample with dimensions of 5 mm × 5 mm × 10 mm [21].

It is important to note that nacre behaves differently when under dry or hydrated conditions. Fig. 1 B represents a typical tensile behaviour of pure aragonite, dry nacre and hydrated nacre. As it is possible to observe, the tensile behaviour of dry nacre is more akin to that of pure aragonite, acting as a brittle material. In contrast, hydrated nacre shows a ductile behaviour. These results evidence not only that water is important for nacre's ductile behaviour, but also demonstrates that the organic materials are essential for nacre's properties, even if they only represent 5% of its composition. Such influence of water can also be observed in other calcium carbonate organizations such as crossed-lamellar sea shells [22]. After analysing this behaviour, Jackson et al. [14] concluded that water plasticizes the organic matrix, which affects the elastic modulus and tensile strength by reducing the matrix's modulus and shear strength, resulting in greater crack blunting and