

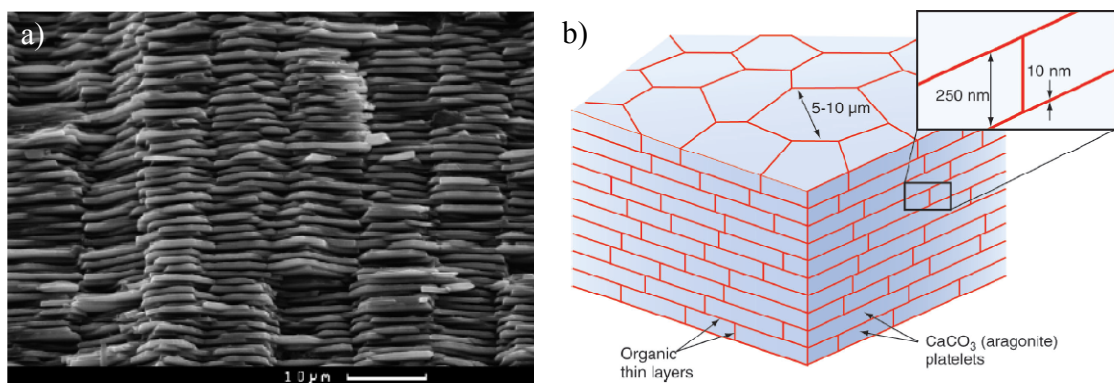
# Artificial Seashells: Multilayered Hybrid Nanocomposites for Improved Mechanical Properties

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Nature has provided us with many examples of biomaterials that possess unique combinations of hardness, stiffness and fracture toughness, many of which remain unattained by manmade monolithic ceramics and composites.<sup>1,2</sup> These biomaterials exhibit well-designed morphologies and hierarchical structures composed of chemically simple materials.<sup>3</sup> One such example is nacre, which is the iridescent layer found inside a large number of mollusk shells. It constitutes a layered arrangement of at least 95 wt % aragonite platelets ( $\text{CaCO}_3$ ) separated by thin, intermediate biopolymer layers consisting of proteins and/or polysaccharides into a brick and mortar structure (Figure 1).<sup>4</sup> Despite being made of an intrinsically soft mineral, nacre is 3000 times tougher than monolithic  $\text{CaCO}_3$ ; measurements show an elastic modulus of 40 - 70 GPa and a strength up to 120 MPa.<sup>5</sup> This enhanced mechanical property is believed to be imparted through nano and microscale structures on the platelets as well as through viscoplastic energy dissipation in the organic layer associated with the controlled sliding of the aragonite layers over each other.<sup>5-8</sup> As such, there have been considerable efforts to mimic the designs and structure of nacre materials with the hope of reproducing these fascinating properties.

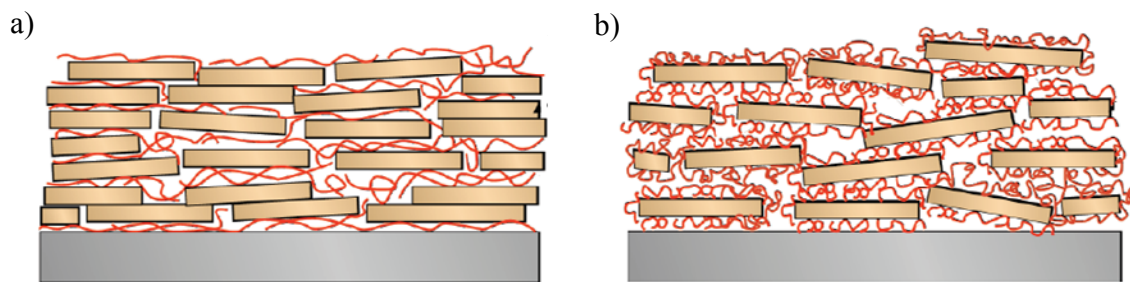


**Figure 1.** (a) SEM of the microstructure of nacre. (b) Schematic diagram of nacreous structure.<sup>3</sup>

The structure of nacre has been mimicked by several approaches, of which layer-by-layer (LbL) and ice templating will be highlighted due to the excellent control over the layer thickness. In LbL, sequential adsorption of nanometer thick monolayers of oppositely charged compounds (such as polyelectrolytes and charged nanoparticles) are deposited onto a glass substrate to form a multilayered structure with nanometer control over the architecture.<sup>9,10</sup> This method has been used to fabricate films composing of alumina platelets and chitosan<sup>11</sup>, as well as poly(diallyldimethylammonium chloride) (PDDA) or poly(vinyl alcohol) (PVA) and montmorillonite (MTM)<sup>2,12</sup> (Figure 2). With PVA and MTM, films of up to  $1.5 \pm 0.1 \mu\text{m}$  thick can be fabricated, which translate to about 300 bilayers of each 5 nm.<sup>12</sup> Although PVA is uncharged, the high efficiency of hydrogen bonding between PVA and MTM and the substantial cross linking of Al substitution present on the surface of MTM to Al atoms along the edges of MTM allows

for a stronger composite as compared to other polymers using electrostatic attraction. When this nanocomposite is cross linked with glutaraldehyde, the tensile strength increased to as high as 380 MPa. Podsiadlo *et al.* has also further showed that the tensile strength and modulus can be improved by adding cations such as  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$ .<sup>13</sup> It is believed this improvement is due to the abundance ionic, hydrogen and van der Waals bonds that can break and reform when the polymer and clay phases slide against each other.

In the ice template method, the formation of pure hexagonal ice platelets is utilized to entrap the dispersed ceramic particles within channels between the ice crystals.<sup>14</sup> Through a freeze-casting process which involves the controlled unidirectional freezing of ceramics suspension, an ice templated, porous, layered material with layers as thin as 1  $\mu\text{m}$  is first fabricated.<sup>15</sup> These porous scaffolds are then filled with a selected second phase to fabricate dense composites. This method allows for the fine tuning of the micro and macro-structure to give lamellar or brick-and-mortar structures. It has been found that grafting a methacrylate group onto the ceramic surface before polymethyl methacrylate (PMMA) infiltration acts to promote stronger covalent bonding between the two phases. Large inelastic strains were observed in the brick-and-mortar structure when loaded in tension and were exceptionally tough against crack propagation.



**Figure 2.** Schematic diagram of the (a) LbL method and (b) one step assembly of polymer coated inorganic platelets.<sup>16</sup>

Although remarkable success has been achieved in reproducing biomimetic nacre materials with exceptional mechanical properties, such feats have been limited to the laboratory. Current laboratory methods are time consuming and energy intensive, which makes scaling up is an issue that would need to be addressed for these materials to enter the mainstream market. Walther *et al.* has recently demonstrated a clever method to fabricate these materials by using nanoclay sheets with soft polymer coatings as the building blocks (Figure 2).<sup>16</sup> These core/shell hard/soft monomers can be forced to rapidly self-assemble into aligned nacre-mimetic films via paper-making techniques or simply by painting, giving rise to strong and thick films with tensile modulus of 45 GPa and strength of 250 MPa. By altering the ionic supramolecular bonding using counter ions, the cohesiveness between the layers can be altered to change the stiffness of the materials.<sup>17</sup> In addition to the enhanced mechanical strength, these films exhibit fire-resistance and heat-shielding capabilities of up to 2000 °C.

Hence, by combining two relatively ordinary materials, hybrid biomimetic nacre materials with excellent strength and toughness properties can be fabricated. As we continue to learn and understand how the hierarchical architecture affects the properties of nacre materials, it can be certain that biomimetic nacre materials hold the key to technological advances for the next generation.

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