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MINI REVIEW

Artificial Nacre Nanocomposites for Advanced Applications

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ABSTRACT

Nature has provided us best materials with exceptional properties. In order to develop next-generation new materials with light weight, high-strength, and tough materials, establishment of novel design strategies must be implemented. Nacre, the mother-of-pearl, an organic-inorganic composite material produced by some molluscs that is strong, resilient, and iridescent. Hence mimicking nacre's micro/nanostructure in artificial materials is an alternative way to fabricate high performance structural materials for scientists and engineers. This gives us numerous multifunctional materials with unique properties of stiffness and hardness. Artificial nacres have found enumerable applications in modern day science from flame retardant materials to implanting into biomaterials. This review presents various strategies for making artificial nacre and its uses in advanced applications.

Introduction

Nature has given us with numerous examples of biomaterials, which exhibit fascinating and excellent multifunctionality that possesses unique properties of stiffness, hardness and fracture toughness with the characteristics of self-organizing, self-assembly, self-healing, etc. [1]. Mimicking many of these properties are still remain a challenge by man-made composites. It is to note that only materials on the macroscopic scale can be applied for potential replacement of conventional structural materials. One such example is nacre, the iridescent material found inside a large number of seashells or mollusc shells. The excellent mechanical strength in the nacre originates from the hierarchical micro- and nanostructures [1].

Structure of Nacre

Mollusc shells consist of 95-99% of calcite or aragonite as a major constituent and 0.1-5% of organic materials in the form of polysaccharides and proteins as shown in Figure 1 [2,3]. The hierarchical structure consists of organic and inorganic, though being made of an intrinsically soft material; nacre is 3000 times higher than the monolithic aragonite platelets (CaCO3). This enhances mechanical strength is due to the nano/microstructures of the platelets and also due to the viscoelastic energy dissipation in the organic layers associated with the controlled sliding. There have been many synthetic methods for mimicking various kinds of natural structures either organic or inorganic at the micro/nanoscale. Biomaterials have been made by different strategies, in particular artificial nacre, where the organic matrix plays a major role [4].

Nacre can be viewed in many dimensions such as 1D nacre-inspired fibres, 2D nacre-inspired films, and 3D nacre-inspired bulk composites [5]. Though these materials are high in demand but still the applications are limited and needs to be explored for future prospects.

Design strategies

Nacre-like structures from nanoplatelets/sheets: Using the nanoplatelets and polymers, a high-strength and highly transparent nacre-like nanocomposites have been prepared via layer-by-layer assembly technique, for example, poly (vinyl alcohol) (PVA) and Na$^+$-Montmorillonite (Na MMT) clay nanosheets, which are strong, flexible, but also highly transparent.

Purely inorganic artificial nacre has been prepared by controlled evaporation technique. Pujala et al. have prepared nacre-like structures from Na$^+$-Montmorillonite and Laponite with hierarchical structures of clay platelets using this method [6,7]. They have also demonstrated that the transparency and the structural ordering of the films can be tuned by playing with the mixing ratios. Artificial nacres films are formed by solution casting methods and also by slow evaporation of soft gels. The ordering of the platelets is not disturbed by the presence of nano/microspheres and it displays numerous interesting features such as mechanical strength and flexibility of the nacre-like films [6,7].

There have been numerous approaches to produce structurally ordered composites with structure and mechanical properties similar to those of natural nacre [8]. Macroscopic nacre-like composite materials can be prepared from hot-press assisted slip casting, freeze casting biomineralization or bottom-up approach [9], extrusion and roll compaction, solution and gel-casting methods. Clay nanosheets and graphene based artificial nacre have been extensively studied due to its availability and biocompatibility. Sarin et al. produced chitosan/clay nanoplatelets materials via charge based self-assembly mediated progressive, in situ charging of chitosan. [10]. Das et al. used poly (vinyl alcohol) (PVA) and clay nanoplatelets of multiple aspect ratios to produce glass-like transparency, excellent gas barrier properties, and excellent mechanical properties via concentration induced self-assembly. Smaller platelets resulted in Materials with smaller platelets gave rise to stiffer materials than the large aspect ratios [11].

Nacre-like structures from grapheme: Graphene has attracted lot of interest recently as a biomaterial due to its electrical conductance, biocompatibility, bioactivity, and has potential for surface modification. Graphene is an ideal candidate as it is tailorable nanomaterial, for the ceramic phase in nacre mimetic materials. Wan et al. fabricated conductive and strong nacre-like structures using vacuum assisted filtration to align graphene oxide (GO) [12]. High tensile strength and toughness of graphene was achieved by nanofibrillar cellulose. The impressive mechanical properties were due to the breakage of hydrogen bonds [13]. Nacre-mimetic materials with multifunctional properties and excellent mechanical properties can be obtained by combining ceramics and polymeric phases that exhibits with enhanced electrical conductance, fluorescence and optical transparency.

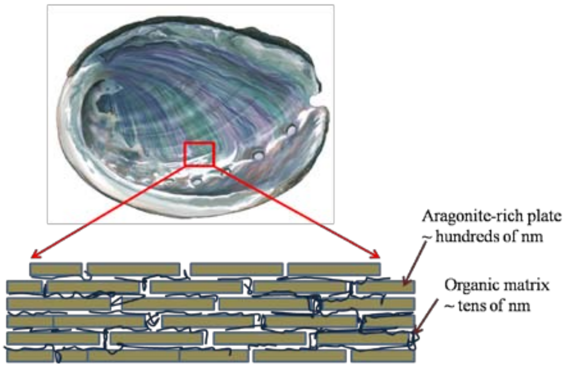

Figure 1: Schematic of nacre with brick-and-mortar like structure, in which hard aragonite-rich plates are glued together with soft organic matrix to form tiles.

Nacre-like bionanocomposites: Although the major component of the nacre composed of more than 95 wt% inorganic aragonite, the organic component (0.1-5% (w/v)) is vital not only to the excellent mechanical properties but particularly for the bioactivity and biocompatibility of the nacre [14]. The organic material forms the framework between the inorganic mineral phases. It is composed of beta – chitin, silk-like proteins, and acidic glycoproteins rich in aspartic acid. The use of organic matrix has been the subject of extensive research [15]. This decides the bioactivity, biocompatibility, osteogenic activity and biodegradability of nacre.

Applications of artificial nacre

Nacre-inspired composites represent alternatives for replacing traditional engineering materials, such as plastics, alloys and ceramics due to their exceptional mechanical and thermal properties. Additionally, for potential applications in the fields of electric cables, fire-retardant materials, gas barriers, nanogenerators, and supercapacitors, modification of high mechanical performance materials has to be done to achieve nacre-inspired materials (Figure 2) [16-20]. Graphene oxide-carrageenan (GO-Car) nanocomposite films are promising materials for the replacement of traditional petroleum-based plastics and also as tissue engineering-oriented support materials [21]. Nanocomposite film based on 2D graphene (G), nanosheets and 1D carbon nanotubes (CNTs) and nanofibrillated cellulose (NFC) prepared from casting method showed superior water resistance and great potential in practical applications [22].

Due to its biocompatibility, mechanical strength, bioactivity and biodegradability of nacre-based biomaterials, and also additional properties such as fluorescence ability, nacre can be utilized as a biomaterial in a variety of applications as shown in Figure 2. Major applications of nacre-based biomaterials include:

(a) Use of nacre material directly as a bone substitute or in the bone defects [23].

(b) As a coatings for implants and drug delivery vehicles. This is done to improve the biocompatibility of implants by means of physical or biological methods.

(c) Injection of nacre matrix into bone defects.

(d) Nacre-like Nanomaterial, fluorescent material within soft materials [24].

(e) Used as Osteogenic additives. Nacre nanocomposites can be used in the field of nanotechnology and also as novel nanocarriers. They can be used as implants in vivo [25].

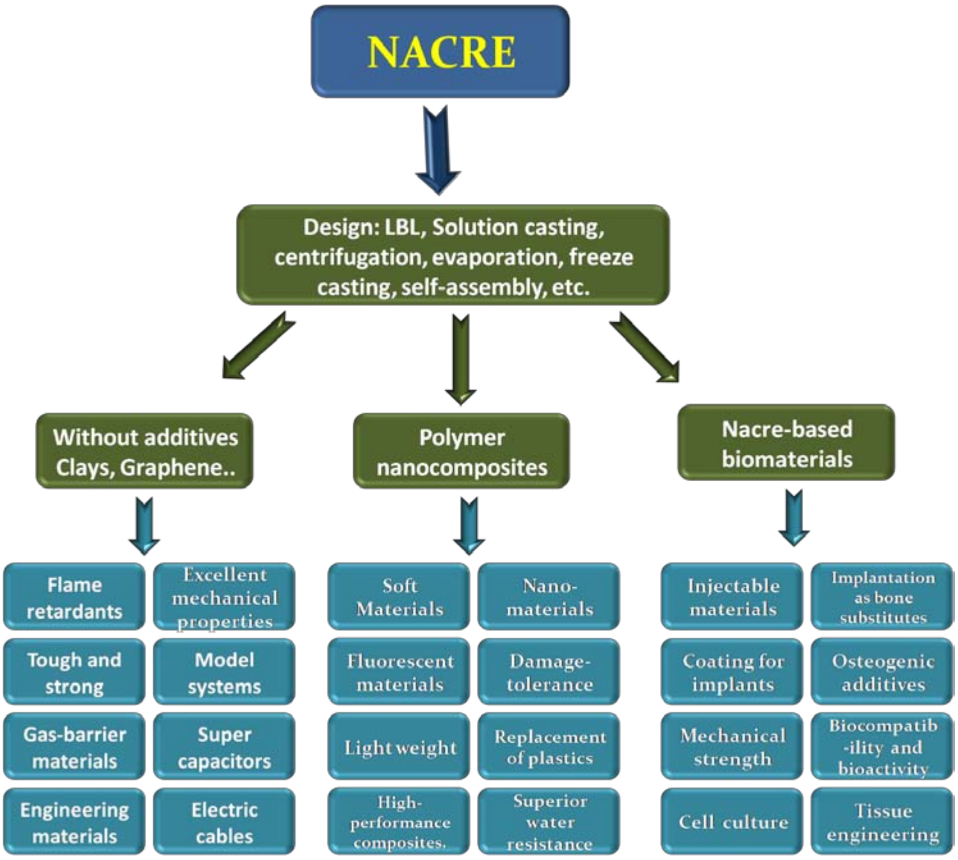

Figure 2: Design and applications of nacre-based materials. Application of inorganic (without additives), polymer nanocomposites and bionanocomposites are shown.

Conclusion

An efficient approach to attain high mechanical and structured materials in artificial materials is achieved by mimicking nacre's hierarchical brick-and-mortar structure. Artificial nacre materials were synthesized by different strategies such as layer-by-layer (LBL), centrifugation, hot-pressing and evaporation methods. In this review, we summarized recent achievements in nacre-inspired bio- and nanocomposites and other novel strategies for further improvement in their mechanical, thermal and electrical properties. Nacre-like materials with better performance will be achieved with clear understanding of the relationship between structure and properties. Their applications will be broadened in the near future in the fields or soft matter, nanomaterials, biomaterials. They are the efficient replacement for the plastic, alloys, ceramics, bones, coating for the implants and Injectable materials. However, there is lot of scope for improving their mechanical strength, bioactivity and biocompatibility. Thus, these nacre-based new materials are a subject of greater interest currently, and many studies are being dedicated to explore the structure and its future applications.

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References

1. Mayer G. (2005). Rigid biological systems as models for synthetic composites. Science 310: 1144-1147.
2. Wegst UGK, Bai H, Saiz E, Tomsia AP, Ritchie RO. (2015). Bioinspired structural materials. Nat. Mater. 14: 23-36.
3. Wang J, Cheng Q, Tang Z. (2012). Layered nanocomposites inspired by the structure and mechanical properties of nacre. Chem. Soc. Rev. 41: 1111-1129.
4. Barthelat F, Yin Z, Buehler MJ. (2016). Structure and mechanics of interfaces in biological materials. Nat. Rev. Mater. 1: 16007.
5. Zhao H, Yang Z, Guo L. (2018). Nacre-inspired composites with different macroscopic dimensions: strategies for improved mechanical performance and applications. NPG Asia Materials 10: 1-22.
6. Pujala RK, Schneijdenberg CTWM, van Blaaderen A, Bohidar HB. (2018). In-situ Observation of Hierarchical Self-Assembly Driven by Bicontinuous Gelation in Mixed Nanodisc Dispersions. Scientific Reports. 8: 5589.
7. Pujala RK, Kumar MP, Dhara S. (2018). Hierarchical self-assembly of colloidal nanoplatelets driven by evaporation. J. Phys. D: Appl. Phys. 51: 30.
8. De Luca F, Menzel R, Blaker JJ, Birkbeck J, Bismarck A, et al. (2015). Nacre-nanomimetics: Strong, Stiff, and Plastic. ACS Appl. Mater. Interfaces 7: 26783.
9. Deville S, Saiz E, Nalla RK, Tomsia AP. (2006). Freezing as a path to build complex composites. Science 311: 515-518.
10. Sarin S, Kolesnikova S, Postnova I, Ha CS, Shchipunov Y. (2016). Bionanocomposite from self-assembled building blocks of nacre-like crystalline polymorph of chitosan with clay nanoplatelets. RSC Adv. 6: 33501-33509.
11. Das P, Malho JM, Rahimi K, Schacher FH, Wang B, et al. (2015). Nacre-mimetics with synthetic nanoclays up to ultrahigh aspect ratios. Nat. Commun. 6: 5967.
12. Wan S, Peng J, Li Y, Hu H, Jiang L, et al. (2015). Use of synergistic interactions to fabricate strong, tough, and conductive artificial nacre based on graphene oxide and chitosan. ACS Nano. 9: 9830-9836.
13. Duan J, Gong S, Gao Y, Xie X, Jiang L, et al. (2016). Bioinspired ternary artificial nacre nanocomposites based on reduced graphene oxide and nanofibrillar cellulose. ACS Appl. Mater. Interfaces 8: 10545-10550.
14. Levi-Kalisman Y, Falini G, Addadi L, Weiner S. (2001). Structure of the nacreous organic matrix of a bivalve mollusk shell examined in the hydrated state using cryo-TEM. J. Struct. Biol. 135: 8-17.
15. Kröger N. (2009). The molecular basis of nacre formation. Science. 325: 1351-1352.

16. Cruz-Silva R, Aaron Morelos-Gomez, Hyung-ick Kim, Hong-kyu Jang, Ferdinando Tristan, et al. (2014). Super-stretchable graphene oxide macroscopic fibers with outstanding knotability fabricated by dry film scrolling. ACS Nano. 8: 5959-5967.

17. Walther A, Ingela Bjurhager, Jani-Markus Malho, Jaakko Pere, Janne Ruokolainen, et al. (2010). Large-area, lightweight and thick biomimetic composites with superior material properties via fast, economic, and green pathways. Nano Lett. 10: 2742-2748.

18. Choi JH, Young Wook Park, Tae Hyun Park, Eun Ho Song, Hyun Jun Lee, et al. (2012). Fuzzy nanoassembly of polyelectrolyte and layered clay multicomposite toward a reliable gas barrier. Langmuir. 28: 6826-6831.

19. Guo W, Cheng C, Wu Y, Jiang Y, Gao J, et al. (2013). Bio-inspired two-dimensional nanofluidic generators based on a layered graphene hydrogel membrane. Adv. Mater. 25: 6064-6068.

20. Yang X, Zhu J, Qiu L, Li D. (2011). Bioinspired effective prevention of restacking in multilayered graphene films: towards the next generation of high-performance supercapacitors. Adv. Mater. 23: 2833-2838.

21. Zhu W, Chen T, Li Y, Lei J, Chen X, et al. (2017). High Performances of Artificial Nacre-Like Graphene Oxide-Carrageenan Bio-Nanocomposite Films. Materials. 10: 536.

22. Jin S, Li K, Li J. (2018). Nature-Inspired Green Procedure for Improving Performance of Protein-Based Nanocomposites via Introduction of Nanofibrillated Cellulose-Stablized Graphene/Carbon Nanotubes Hybrid. Polymers. 10: 270.

23. Rodrigues JR, Alves NM, Mano JF. (2017). Nacre-inspired nanocomposites produced using layer-by-layer assembly: design strategies and biomedical applications. Mat. Sci. Eng. 76: 1263-1273.

24. Li X, Pan D, Lin S, Zhuang Z, Lin Z. (2013). Facile in vitro hydroxyapatite remineralization of human enamel with remarkable hardness. CrystEngComm. 15: 4351-4356.

25. Liao H, Mutvei H, Sjöström M, Hammarström L, Li J. (2000). Tissue responses to natural aragonite (Margaritifera shell) implants in vivo. Biomaterials. 21: 457-468.