

Bioinspired Layered Materials with Superior Mechanical Performance

Via Interface Design

Qunfeng Cheng^{*a}, Lei Jiang^a and Zhiyong Tang^b

a. Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, P. R. China, Fax: 86-10-82313981, Tel: 86-10-82316171, E-mail: cheng@buaa.edu.cn

b. Key National Center for Nanoscience and Technology, Beijing 100190, PR China.

ABSTRACT

Inspired from nature, orderly layered structure, has been broadly accepted to be very effective candidate to construct high mechanical performance materials. Herein, we summarize our recent research work and outstanding representative progress from other groups in the interface design of the bioinspired layered materials composed of varying primitive materials. The interface designs for bioinspired layered materials are generally categorized into: (1) hydrogen bonding, (2) ionic bonding, and (3) covalent bonding. Altogether, we demonstrate that these interface design strategies are significant for constructing high performance bioinspired layered materials as well as offer innovative insights into production of functional artificial materials.

Keywords: bioinspired; layered materials; interface; mechanical properties

1 INTRODUCTION

After billions of years of evolution, two types of materials with dissimilar mechanical properties, inorganic minerals of high strength but low ductility and organic macromolecules of good ductility but bad strength, could be successfully integrated into the hierarchical micro-/nano-scale layered structure, showing the unique mechanical performance. A typical example is abalone nacre.^[1] It has been explored that 95% volume fraction of the nacre is aragonite calcium carbonate platelets, which are orderly assembled into the micro-/nano-scale layered structure with help of about 5% organic biopolymer binders, giving rise to combination of the strength and toughness of the nacre. The excellent mechanical property of the nacre well embodies the advantage of both the orderly layered structure and the abundant interface between inorganic platelets and organic matrix.

Inspired by both the structural and mechanical characteristics, scientists have tried a variety of approaches to mimic the natural nacre and build the nacre-like layered composites. It should be pointed out that the excellent mechanical properties of the abalone nacre and their ingenious microstructure have been well introduced in

recent excellent reviews,^[2] and will not be included in this study. Herein, the discussion is focused on the interface design of the bioinspired layered materials consisted of different primitive materials based on our recent research progress. Simultaneously, some other important works on the interface design of the nacre-like materials are also summarized.

2 RELATIONSHIP OF UNIQUE MECHANICAL PROPERTIES AND LAYERED STRUCTURE OF NACRE

Generally, a typical 3D brick-and-mortar structure is discerned in the nacre (Figure 1A),^[3] in which the aragonite calcium carbonate microplatelets of 5~8 μm in diameter and ~0.5 μm in thickness are orderly stacked together through the rough contact surfaces instead of the smooth planes. High resolution imaging reveals that the surfaces of the microplatelets are consisted with many nanoasperities of 10-30 nm in width and 100-200 nm in spacing, while these microplatelet tiles are connected by the mineral bridges that are embedded in the organic layers (the third image from top in Figure 1A). Furthermore, the fibrous chitin networks are found to form the backbone of the organic layers (the bottom image in Figure 1A). Notably, the natural nacre shows the typical two level of micro-/nano-scale hierarchical layered structures. The first level is that calcium carbonate nanograins are glued together to form the microplatelets. The second level is brick-and-mortar structure that is formed by the staggered microplatelets with biopolymer. To obtain more detailed information about the architectures of the nacre, readers can refer to the previous reviews. The tensile strength and Young's modulus of the nacre is in the range of 80-135 MPa and 60-70 GPa,^[4] respectively, depending on the wet or dry states, which give rise to the tensile toughness of around 1.8 MJ/m³ calculated by integrating area underneath the stress-strain curve. The detailed tensile stress-strain curve of the nacre is shown in Figure 1B, with a maximum strength of 80 MPa and a large plastic deformation. At a threshold stress of 70 MPa, the organic constituent starts to yield and the microplatelets locally slide on one another. The nacre finally fractures in the form of the microplatelet pull-out mode. One of the prominent mechanical properties of the nacre is toughness, which can be estimated by the

fracture testing (Figure 1C). Different from the tensile toughness that represents the deformation energy of the materials, the fracture toughness describes the ability of a material containing a crack to resist fracture, with the unit of $\text{Pa}\cdot\text{m}^{1/2}$ for linear-elastic fracture toughness and the unit of J/cm^2 for plastic-elastic fracture toughness, respectively. With the field stress is increased on the nacre, a white region appears and progressively expands along the crack embedded in the region. The crack resistance curves of the nacre further indicate that the toughness increases significantly with the crack advancing. The fracture toughness of the nacre can reach $1.5 \text{ KJ}/\text{m}^2$, which is about 3000 times higher than that of pure calcium carbonate platelets ($\sim 0.5 \text{ J}/\text{m}^2$).

These unique mechanical properties are attributed to the micro-/nano-scale hierarchical layered structure and the precise interface pattern of the nacre, which inspire the scientists and engineers to fabricate the high performance bulk materials through mimicking their structural features.

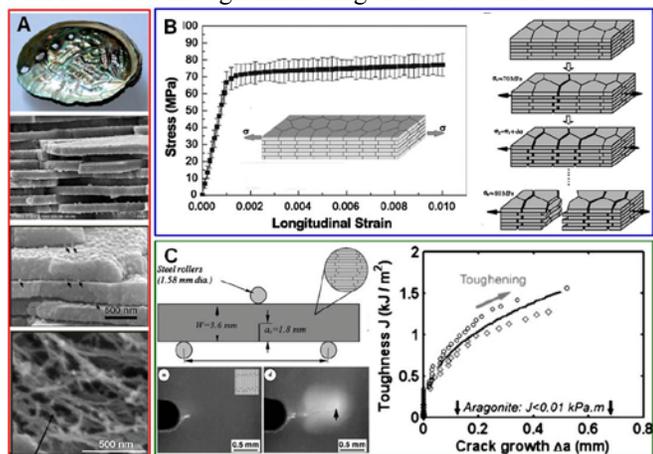


Fig. 1 Relationship of unique mechanical properties and layered structure of nacre. (A) Hierarchical structures of abalone nacre: micro-/nano-scale multilayers.^[3] (B) Typical stress-strain curve of abalone nacre. (C) Single edge notch bending specimen used for fracture testing, and crack resistance curves for nacre from two experiments.^[2]

3 INTERFACE DESIGN OF BIOINSPIRED LAYERED MATERIALS

The representative interface design approaches for the bioinspired layered materials can be categorized into three classes: hydrogen bonding, ionic bonding and covalent bonding (Figure 2). Hydrogen bonding is a typical non-covalent cross-linking mode, affording the soft interfaces between the inorganic plates and the organic matrix. As for the covalent cross-linking, the chemical bond is formed between the inorganic plates and organic matrix, which supplies much stronger interfaces. Typically, the interface strength formed by ionic bonding is higher than that of hydrogen bonding but little lower than that of covalent bonding. In the following sections, different interface design strategies will be discussed in detail.

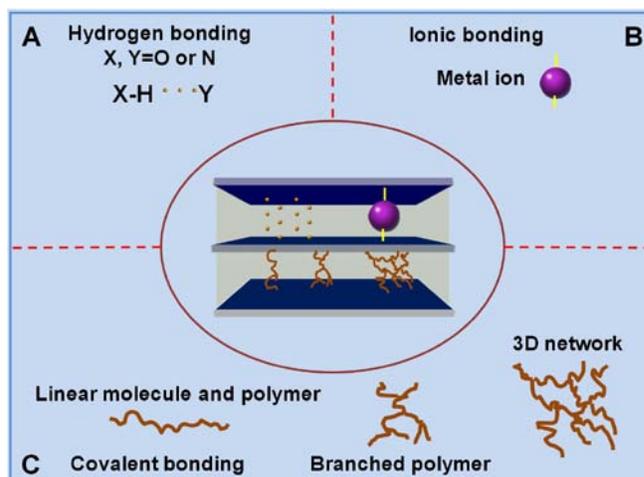


Fig. 2 Illustration of interface design of bioinspired layered materials: (A) Hydrogen bonding. (B) Ionic bonding, such as Mg^{2+} , Ca^{2+} , and B^{3+} . (C) Covalent bonding, containing the linear molecule, branched polymer and thermosetting resin 3D network.

3.1 Hydrogen bonding

Conceptually, the hydrogen bonding, a special type of dipole forces, refers to the interaction between a hydrogen atom, which is attached to an electronegative atom of one molecule, and an electronegative atom of a different molecule. The electronegative atoms are diverse, and could be oxygen, nitrogen, or fluorine that has a partial negative charge. Ruoff et al. fabricated the high performance layered materials based on the GO nanosheets through hydrogen bonding, called as GO paper.^[5] There are numerous oxygen functional groups on the basal planes and edges of the GO nanosheets, resulting in formation of rich hydrogen bonds between the adjacent GO nanosheets and water molecules. Figure 3A displays the typical layered structure of the GO paper. Impressively, the typical stress-strain curves reveal the high values of the mechanical properties (Figure 3B). The tensile strength is up to 133 MPa, which is comparable to that of the natural nacre, while the average Young's modulus is about 32 GPa, half of the nacre. An interesting phenomenon on the layered GO paper is that the Young's modulus increases with cyclic loading, which is similar to self-reinforcing behavior of the aligned polymer chains and other fibrous materials. Such an increase in the Young's modulus is caused by better alignment of the GO nanosheets through stretching the layered GO paper, leading to improvement of their contact and interaction. The scheme of deformation mechanism at tension and bending (Figure 3C) indicates that the tensile stress is mostly transferred through the shear deformation of the interlamellar hydrogen bonded water molecules, resulting in a homogenous distribution across the layered GO paper; whereas the bending introduces the localized stress at the surface of the layered GO paper. As a result, the delamination is happened along the defects in the layered GO paper due to the transformation of stress at the outer surface by combination of shear and pull-out of the

hydrogen bonded water molecules between the GO nanosheets.

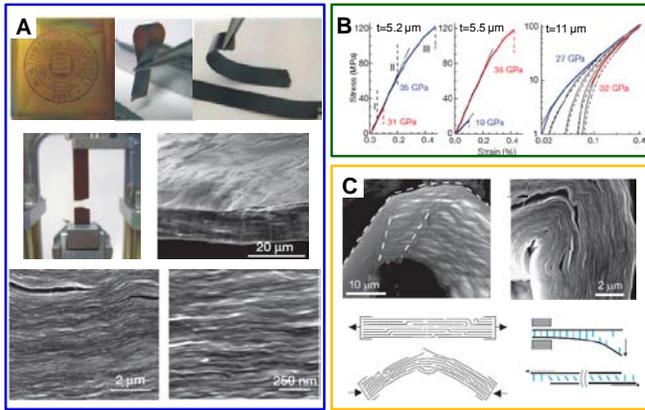


Fig. 3 Hydrogen bonding in the layered GO papers. (A) Photos of GO paper with different thickness, strip after fracture from tensile loading, and the scanning electron microscopy (SEM) side-view images at different resolutions. (B) The stress-strain curves of GO paper with different thicknesses of 5.2 μm and 5.5 μm , and the cyclically loaded stress-strain curve of a sample with thickness of 11 μm . (C) SEM images of curved GO paper, and the schematic drawings of uniaxial in-plane loading to fracture and a bending to buckling test.^[5]

3.2 Ionic bonding

Compared with the hydrogen bonding, the ionic bonding needs higher energy to be ruptured, which will be better for improvement of the mechanical strength of resultant materials. Tang et al. took advantage of the ionic bonding to strengthen the bioinspired layered materials.^[6] The calcium ion bonding is formed between nanoclay and poly(diallyldimethylammonium) (PDDA) chloride polyelectrolyte, leading to the tensile strength increasing from 110 MPa to 152 MPa without noticeable change in Young's modulus. Park et al. introduced the ionic bonding in the GO paper.^[7] The GO nanosheets are bound with the small amount (less than 1 wt%) of metal ions including Mg^{2+} and Ca^{2+} . The edge-bound metal ions bridge the carboxylic acid groups on two adjacent GO nanosheets, which can resist normal deformation between the GO nanosheets. Therefore, the tensile strength and Young's modulus of the layered GO paper are increased from 81.9 ± 5.3 MPa and 25.6 ± 1.1 GPa to 125.8 ± 13.6 MPa and 28.1 ± 1.2 GPa, respectively, after Ca^{2+} cross-linking.

3.3 Covalent bonding

Recently, Nguyen et al. constructed the layered GO materials of the largest stiffness through borate orthoester covalent bonding.^[8] The idea is inspired by the structural rigidity of maize (*Triticum aestivum*) plants, where borate is key to reinforce the intercellular structure via cross-linking of the structural polysaccharide rhamnogalacturonan II (RG II) (Figure 4A). When introduction of only 0.94 wt% borate ions into the layered GO materials, the borate oligo-orthoesters are formed with

the GO nanosheets through the hydroxyl moieties on the GO surface (Figure 4B). The tensile strength is increased from 130 ± 18 MPa to 160 ± 18 MPa, corresponding to 25% improvement. Simultaneously, the storage modulus is dramatically enhanced from 30 GPa to 110 GPa, corresponding to 266% improvement. The strength and modulus can be further elevated to 185 ± 30 MPa and 127 ± 4 GPa, respectively, via thermal annealing. The enhancement of the mechanical performance originates from additional covalent bonds as the layered materials are dehydrated. It should be stressed that the formation of the borate oligo-orthoesters at very low borate concentration is unique for the annealed cross-linked materials, which is contrast to the borate ions in plants. The oligomerization may also be responsible for increase in the modulus of the resultant layered materials during annealing, owing to formation of the cross-linking bonds of variable lengths.

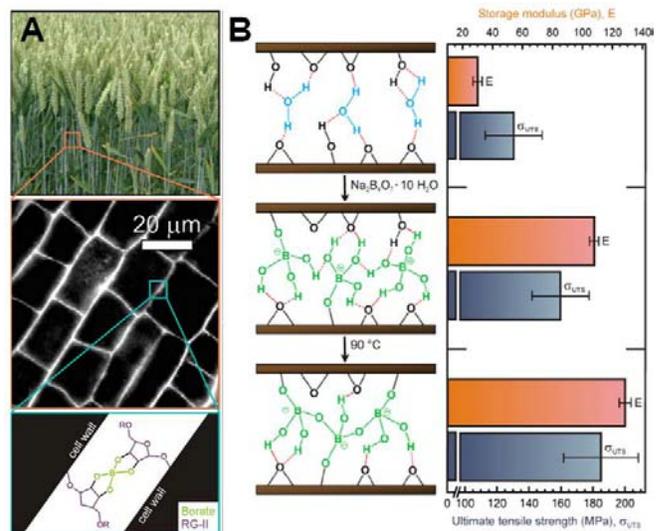


Fig. 4 Interface of borate cross linking in GO papers. (A) Maize (*Triticum aestivum*) plants containing borate to reinforce the intercellular structure via cross-linking of the structural polysaccharide rhamnogalacturonan II (RG II). (B) Scheme of formation of the borate cross-linked network across two adjacent GO nanosheets in the layered materials.^[8]

4 PRINCIPLES OF SELECTING BUILDING BLOCKS FOR LAYERED MATERIALS

It has been proved that the layered structures will dramatically improve the mechanical properties of materials based on different building blocks. In principle, to adopt the high performance of building blocks easily generates the high performance layered materials. Based on our research and other recent reports, the intrinsic mechanical properties of the building blocks and their bioinspired layered materials are summarized in Figure 5. Several typical building blocks, including man-made CaCO_3 platelet,^[9] Al_2O_3 flake,^[10] nanoclay,^[11] CNTs,^[12] and GO nanosheet,^[13] are compared in mechanical properties (Figure 5A). The aragonite platelets in the natural nacre

have a rather low mechanical property with the tensile strength of 334-505 MPa^[14] and the Young's modulus of 50-100 GPa,^[15] respectively. As comparison, the 2D nanoclay possesses the high tensile strength of 500-700 MPa^[16] and the Young's modulus of about 270 GPa.^[17] By using nanoclay as the building blocks, Kotov et al. has demonstrated that the mechanical properties of the clay-PVA bion-inspired layered materials are far higher than that of nacre. The tensile strength reaches 400 MPa, and Young's modulus is as high as 107 GPa. Another typical 2D building block, Al₂O₃ platelet, also has the outstanding mechanic strength including the tensile strength of 330-2000 MPa and the Young's modulus of 300-400 GPa. Based on the Al₂O₃ platelets, Studart et al. fabricated the bion-inspired layered materials with the record-high toughness of 75 MJ/m³ so far.^[10] Ritchie et al. obtained the ultratough layered materials based on Al₂O₃ platelets with the toughness of 30 MPa·m^{1/2}, which is 300 times higher than that of the Al₂O₃ platelets and 10 times higher than that of the natural nacre.^[18] The build blocks based on carbon nanomaterials, such as the GO and the CNTs, possess the prominent tensile strength that is almost two magnitudes higher than that of the above inorganic 2D platelets. For example, the tensile strength and the Young's modulus of the GO is as high as 63 GPa and 500 GPa, respectively; while the experimental results indicate that the tensile strength of the CNTs can reach 100 GPa, and the Young's modulus is as high as 1000 GPa, respectively. Accordingly, we have successfully constructed the bion-inspired layered materials of the highest tensile strength based on the CNTs as well as the ultratough layered materials based on the GO sheets. The maximum tensile strength is up to 1800 MPa, which is one magnitude higher than that of the natural nacre (Figure 5B). Meanwhile, the Young's modulus is as high as 123 GPa, almost two times higher than that of the nacre.^[12] Obviously, the building blocks of the excellent mechanic strength such as carbon-based nanomaterials should be ideal artificial platelets for fabricating the high performance bion-inspired layered materials, even though having the less-elaborate micro-/nano-scale structures with respect to the natural layered structures.

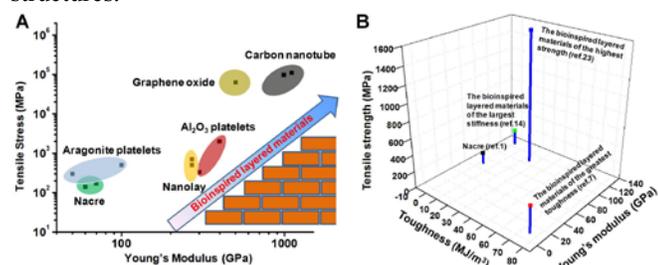


Fig. 5 Mechanical properties comparison of intrinsic building blocks and their bion-inspired layered materials. (A) Typical building blocks. (B) Reprehensive bion-inspired layered materials of prominent mechanical performance.

5 CONCLUSIONS

We reviews recent progress on the interface design of the bion-inspired layered materials based on different building blocks. Three typical categories for the interface design including hydrogen bonding, ionic bonding, and covalent bonding are discussed in details. Thanks to understanding and applying the interface design, many novel bion-inspired layered materials of the high strength, toughness and stiffness have been constructed, making these artificial materials much more possible for practical application in many fields.

REFERENCES

- [1] J. Currey, P. Roy. Soc. Lond. B. Bio. 196, 443, 1977.
- [2] H. D. Espinosa, J. E. Rim, F. Barthelat, M. J. Buehler, Prog. Mater. Sci. 54, 1059, 2009.
- [3] M. A. Meyers, J. McKittrick, P.-Y. Chen, Science 339, 773, 2013.
- [4] A. Jackson, J. Vincent, R. Turner, P. Roy. Soc. Lond. B. Bio. 234, 415, 1988.
- [5] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, Nature 448, 457, 2007.
- [6] Z. Tang, N. A. Kotov, S. Magonov, B. Ozturk, Nat. Mater. 2, 413, 2003.
- [7] S. Park, K. S. Lee, G. Bozoklu, W. Cai, S. T. Nguyen, R. S. Ruoff, ACS Nano 2, 572, 2008.
- [8] Z. An, O. C. Compton, K. W. Putz, L. C. Brinson, S. T. Nguyen, Adv. Mater. 23, 3842, 2011.
- [9] X. Q. Li, H. C. Zeng, Adv. Mater. 24, 6277, 2012.
- [10] A. R. Studart, L. J. Bonderer, L. J. Gauckler, Science 319, 1069, 2008.
- [11] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumphlin, J. Lahann, A. Ramamoorthy, N. A. Kotov, Science 318, 80, 2007.
- [12] Q. Cheng, M. Li, L. Jiang, Z. Tang, Adv. Mater. 24, 1838, 2012.
- [13] Q. Cheng, M. Wu, M. Li, L. Jiang, Z. Tang, Angew. Chem., Int. Ed. 52, 3750, 2013.
- [14] S. P. Kotha, Y. Li, N. Guzelsu, J. Mater. Sci. 36, 2001, 2001.
- [15] B. H. Ji, H. J. Gao, J. Mech. Phys. Solids. 52, 1963, 2004; R. F. S. Hearmon, Rev. Mod. Phys. 18, 409, 1946.
- [16] H. Sato, A. Yamagishi, K. Kawamura, J. Phys. Chem. B 105, 7990, 2001.
- [17] O. L. Manevitch, G. C. Rutledge, J. Phys. Chem. B 108, 1428, 2004.
- [18] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, Science 322, 1516, 2008.