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Bioinspired Layered Materials with Superior Mechanical Performance

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CONSPECTUS: Nature has inspired researchers to construct structures with ordered layers as candidates for new materials with high mechanical performance. As a prominent example, nacre, also known as mother of pearl, consists of a combination of inorganic plates (aragonite calcium carbonate, 95% by volume) and organic macromolecules (elastic biopolymer, 5% by volume) and shows a unique combination of strength and toughness. Investigations of its structure reveal that the hexagonal platelets of calcium carbonate and the amorphous biopolymer are alternatively assembled into the orderly layered structure. The delicate interface between the calcium carbonate and the biopolymer is well defined. Both the building blocks that make up these assembled layers and the interfaces between the inorganic and organic components contribute to the excellent mechanical property of natural nacre.

In this Account, we summarize recent research from our group and from others on the design of bioinspired materials composed by layering various primitive materials. We focus particular attention on nanoscale carbon materials. Using several examples, we describe how the use of different combinations of layered materials leads to particular properties. Flattened double-walled carbon nanotubes (FDWCNTs) covalently cross-linked in a thermoset three-dimensional (3D) network produced the materials with the highest strength. The stiffest layered materials were generated from borate orthoester covalent bonding between adjacent graphene oxide (GO) nanosheets, and the toughest layered materials were fabricated with Al_2O_3 platelets and chitosan via hydrogen bonding. These new building blocks, such as FDWCNTs and GO, and the replication of the elaborate micro-/nanoscale interface of natural nacre have provided many options for developing new high performance artificial materials.

The interface designs for bioinspired layered materials are generally categorized into (1) hydrogen bonding, (2) ionic bonding, and (3) covalent bonding. Using these different strategies, we can tune the materials to have specific mechanical characteristics such as high strength, excellent strain resistance, or remarkable toughness. Among these design strategies, hydrogen bonding affords soft interfaces between the inorganic plates and the organic matrix. Covalent cross-linking forms chemical bonds between the inorganic plates and the organic matrix, leading to much stronger interfaces. The interfaces formed by ionic bonding are stronger than those formed by hydrogen bonding but weaker than those formed by covalent bonding.
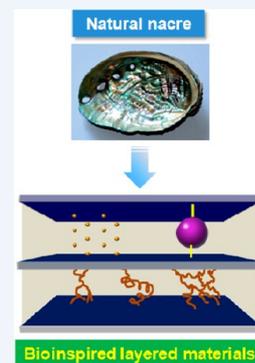
1. INTRODUCTION

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/nanoscale 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/nanoscale 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 been included in this Account. 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 in this Account.

2. RELATIONSHIP OF UNIQUE MECHANICAL PROPERTIES AND LAYERED STRUCTURE OF NACRE

Generally, a typical three-dimensional (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
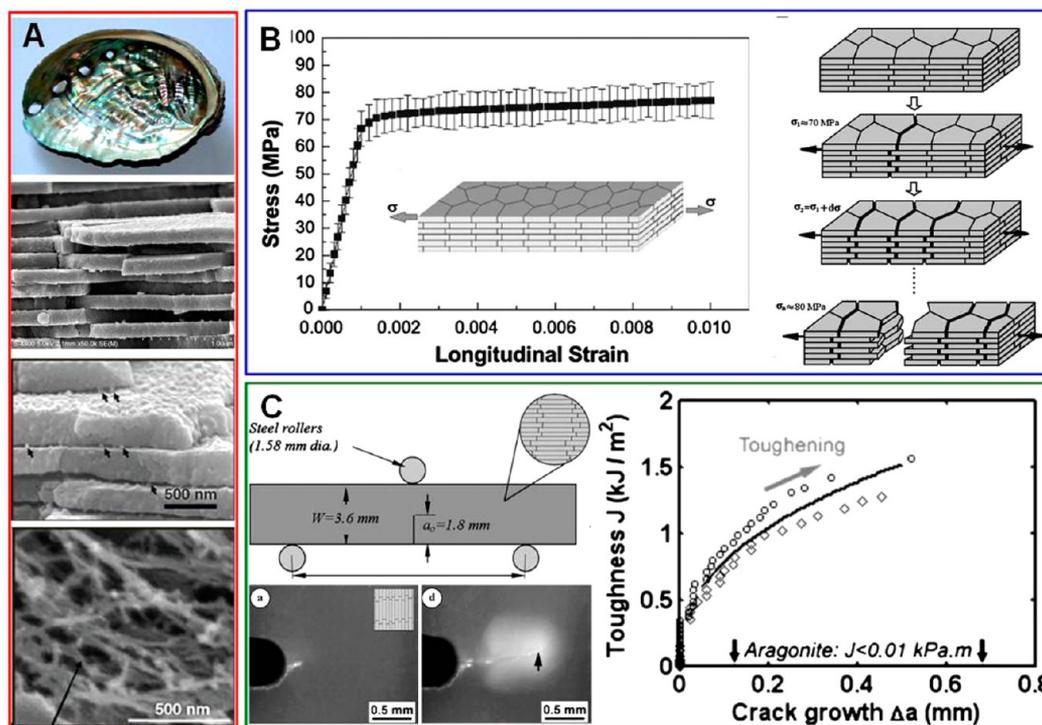
Figure 1. Relationship of unique mechanical properties and layered structure of nacre. (A) Hierarchical structures of abalone nacre: micro/nanoscale multilayers. From ref 3. Reprinted with permission from AAAS. (B) Typical stress−strain curve of abalone nacre. (C) Single edge notch bending specimen used for fracture testing, and crack resistance curves for nacre from two experiments. Reprinted from ref 2, with permission from Elsevier.

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).[3] Notably, the natural nacre shows the typical two level of micro/nanoscale 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 micro-platelets with biopolymer. To obtain more detailed information about the architectures of the nacre, readers can refer to the previous reviews.[2] 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 the 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 mciroplatelets 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 Pa·m^{1/2} for linear-elastic fracture toughness and the unit of J/cm² 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.[2] 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 kJ/m², which is about 3000 times higher than that of pure calcium carbonate platelets (∼0.5 J/m²).

These unique mechanical properties are attributed to the micro/nanoscale 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.

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 noncovalent 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.

3.1. Hydrogen Bonding

Conceptually, the hydrogen bonding, a special type of dipole force, 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 GO paper.[5] There are numerous oxygen functional groups on the basal
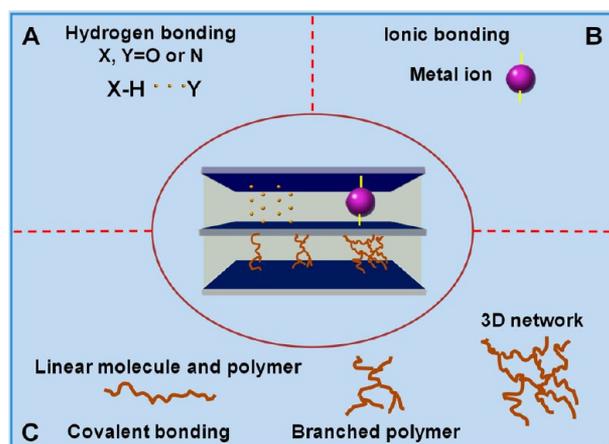
Figure 2. Illustration of interface design of bioinspired layered materials: (A) Hydrogen bonding. (B) Ionic bonding, such as Mg^{2+}, Ca^{2+}, and B^{3+}. (C) Covalent bonding, containing the linear molecule, branched polymer and thermosetting resin 3D network.

planes and edges of the GO nanosheets,[6] 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 that 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 homogeneous 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.

The hydrogen bonding is easily formed among the linear polymers with lots of hydroxyl, carbonyl, or amino groups such as chitosan. Studart et al. prepared the toughest bioinspired layered materials based on Al_2O_3 platelets and chitosan with help of hydrogen bonding.[7] The silane modified Al_2O_3 platelets have many amine groups on their surface, which are assembled into the layered materials through multiple cycles of spin
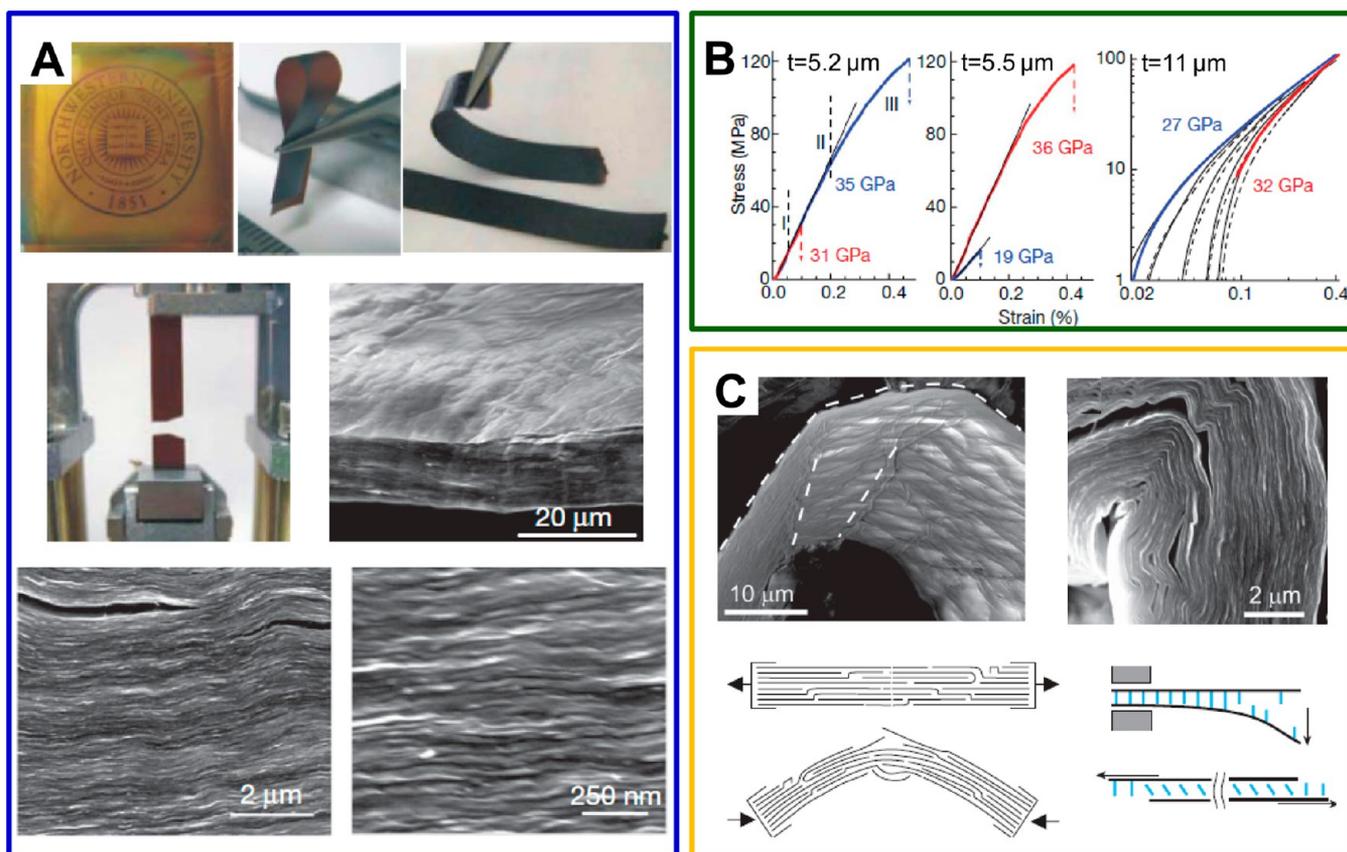
Figure 3. Hydrogen bonding in the layered GO papers. (A) Photos of GO paper with different thickness, strip after fracture from tensile loading, and the scanning electron microscopy (SEM) side-view images at different resolutions. (B) Stress–strain curves of GO paper with different thicknesses of 5.2 and 5.5 μm, and 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. Reprinted with permission from ref 5. Copyright 2012 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

coating with chitosan (Figure 4). Abundant hydrogen bondings are formed between amine groups of silane modified Al_2O_3
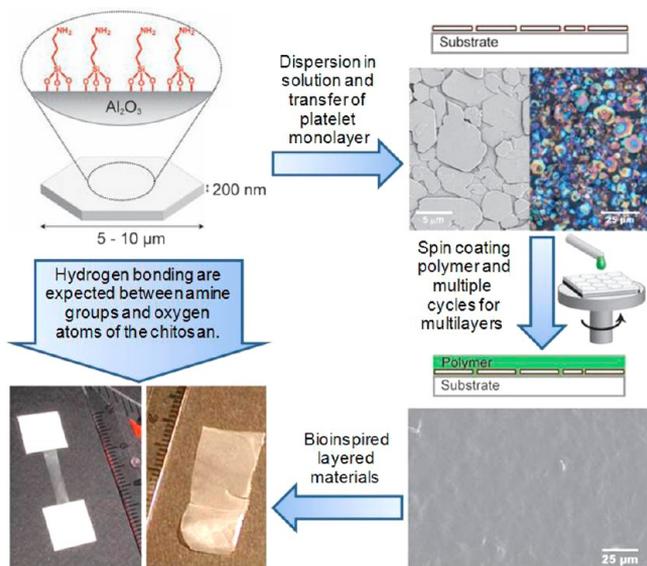
Figure 4. Hydrogen bonding in the Al_2O_3/chitosan layered materials. As shown in the fabrication process, the strong interface of hydrogen bonding is formed between amine groups at the end of the silane hydrophobic tails and the oxygen atoms of the chitosan backbones. From ref 7. Reprinted with permisson from AAAS.

platelets and the oxygen atoms of the chitosan backbone, giving rise to the tensile strength up to 315 MPa and the toughness as high as 75 MJ/m^3. Notably, the obtained toughness is about 42 times higher than that of the natural nacre and 2 orders of magnitude higher than that of the clay-based nanocomposites.[8]

Other linear polymers with hydroxyl groups or oxygen groups, such as poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA), are also the ideal organic partners of rich hydrogen bonds in the bioinspired layered materials. Putz et al. fabricated the layered materials based on PVA, PMMA, and GO nanosheets through hydrogen bonding.[9] For the hydrophilic PVA polymer, the hydrogen bonds are formed between the pendant hydroxyl groups of PVA chains and the oxygen-containing groups (epoxide and carboxyl) on the GO surface. In the layered composites of PVA and GO, the hydroxyl groups of PVA act as both hydrogen bond acceptors and donors, thus enhancing the strength of the resultant materials. Different with the GO-PVA layered materials, the modulus of the GO-PMMA layered materials remains relatively independent of GO loading. This is because the hydrophobicity and steric hindrance of the methyl groups on the PMMA methacrylate side chains impede formation of hydrogen bond between GO and PMMA. Li et al. reported a promising result about the GO-PVA layered materials through hydrogen bonding.[10] The tensile strength reaches 118 MPa with a GO loading amount of 80 wt %, considerably higher than the previous value of 80.2 MPa with GO loading of 60%.[9] It is also surprising that the reduced GO-PVA layered materials possess
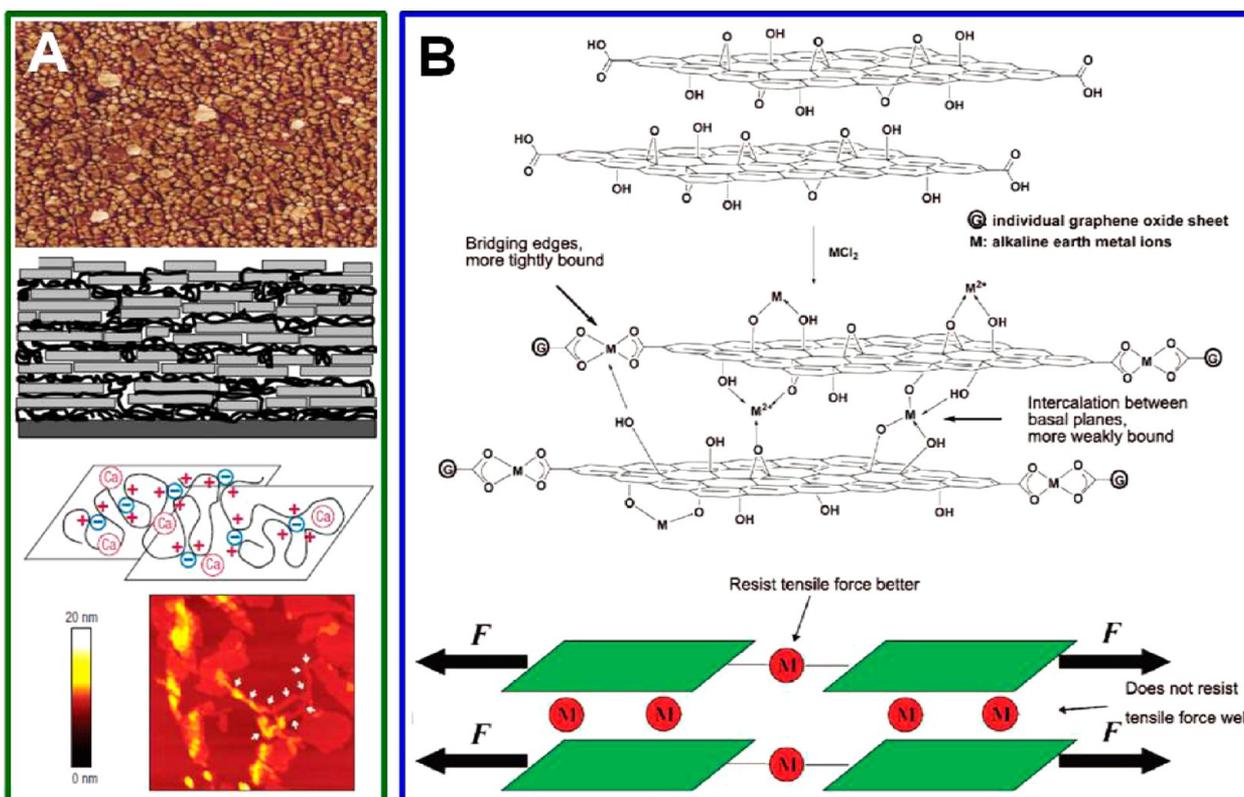
Figure 5. Ionic bonding. (A) Folded PDDA chains and formed ion pairs between PDDA and nanoclay, which are discerned by the topographic AFM images of PDDA molecules adsorbed on the nanoclay platelets. Reprinted by permission from Macmillan Publishers Ltd: *Nat. Mater.* (ref 12), copyright 2003. (B) Scheme of the GO paper with metal ionic bonding: reactions between GO paper and MCl_2 (M = Mg^{2+} and Ca^{2+}) and the proposed model for the enhanced mechanical properties of GO paper after metal ion binding. Reprinted with permission from ref 13. Copyright 2008 American Chemical Society.
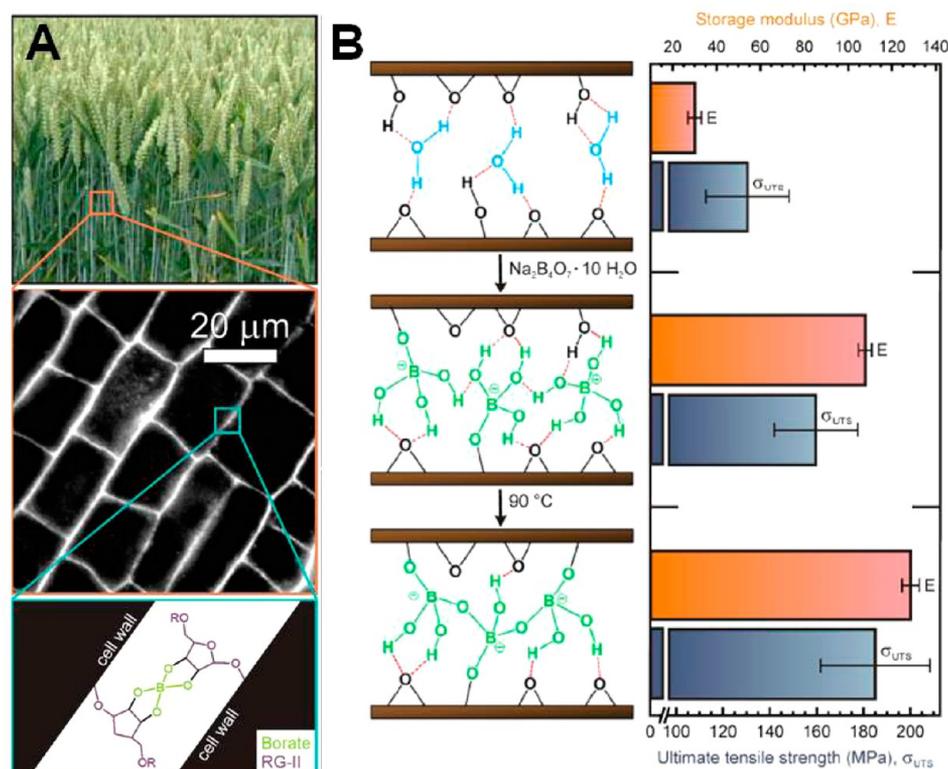
Figure 6. Interface of borate cross-linking in GO papers. (A) Maize (*Triticum aestivum*) plants containing borate to reinforce the intercellular structure via cross-linking of the structural polysaccharide rhamnogalacturonan II (RG II). (B) Scheme of formation of the borate cross-linked network across two adjacent GO nanosheets in the layered materials. Reprinted with permission from ref 14. Copyright 2011 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

even higher mechanical properties, and the tensile strength of the reduced GO-PVA composites reaches 188.9 MPa. The underlying reason why the high mechanical property can be obtained after reducing the GO-PVA composites needs future study.

Apart from the above linear polymers, we also demonstrated successful reinforcement of the layered hydrogel by using hydrogen bonding.[11] The layered clay-poly(*N*-isopropylacryamide) (clay-PNIPAM) hydrogel films are prepared through vacuum infiltration. The hydrogen bonds are easily formed between the PNIPAM and the nanoclay surface, owing to lots of the amide side groups on the PNIPAM and the SiOH or Si—O groups on the nanoclay surface. The bioinspired layered hydrogel shows good combination of tensile strength and toughness. The tensile strength of the layered caly-PNIPAM hydrogel with 23.2 wt % nanoclay reaches 1.6 MPa, and the toughness is as high as 7.38 MJ/m^3 that is 4 times higher than that of the natural nacre. When the interfaces yield, the PNIPAM and the nanocaly extensively slide against each other. The hydrogen bonds between the coiled PNIPAM polymer and the nanoclay surface dissipate the huge energy in the fracture process, resulting in a remarkable toughness.

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.[12] As shown in Figure 5A, the calcium ion bonding is formed between nanoclay and poly(diallydimethylammonium) (PDDA) chloride polyelectro-

lyte, leading to the tensile strength increasing from 110 to 152 MPa without noticeable change in Young's modulus. Park et al. introduced the ionic bonding in the GO paper.[13] The GO nanosheets are bound with the small amount (less than 1 wt %) of metal ions including Mg^{2+} and Ca^{2+}, and the chemical model is illustrated in Figure 5B. 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

3.3.1. Linear Molecule and Polymer. Ionic bonding usually has some intrinsic disadvantages, for instance, easy destruction in solution upon addition of the salts or change of pH value due to screening of the electrostatic attractions. As comparison, the covalent bonding is much more robust, and many linear molecules or polymers are used to help formation of the covalent bonding in the layered materials.

Recently, Nguyen et al. constructed the layered GO materials of the largest stiffness through borate orthoester covalent bonding.[14] 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 6A). With 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 6B). The tensile strength is
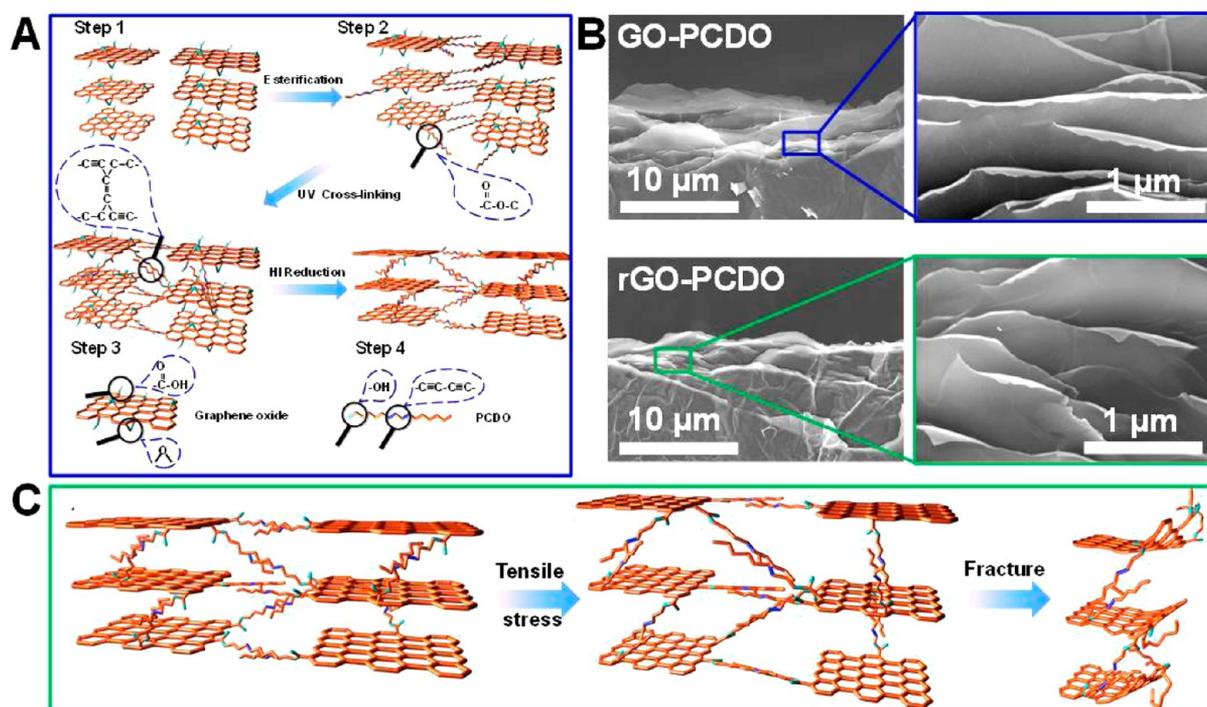
Figure 7. Linear polymer for covalent bonding in the bioinspired layered materials. (A) Fabrication procedure of the bioinspired layered materials based on GO and 10,12-pentacosadiyn-1-ol (PCDO). (B) SEM images, revealing the fracture surface morphology of the PCDO cross-linked GO layered materials. (C) Proposed mechanism of the fracture procedure of the PCDO cross-linked GO layered materials. Reprinted with permission from ref 16. Copyright 2013 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

increased from 130 ± 18 MPa to 160 ± 18 MPa, corresponding to 25% improvement. Simultaneously, the storage modulus is dramatically enhanced from 30 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 case of 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.

A linear small molecule, glutaraldehyde (GA), was introduced to covalently cross-link the adjacent GO nanosheets by Gao et al.[15] Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) results confirm that the aldehyde groups of the GA molecules react with the hydroxyl groups on the surface of the GO nanosheets via intermolecular acetalization.[8] The Young's modulus is enhanced to ∼30.4 GPa from 10.5 GPa, while the tensile strength reaches 101 MPa from 63.6 MPa for as-received GO paper; however, the toughness is only ∼0.3 MJ/m^3, which may be caused by the short GA chains.

We successfully adopted a long chain linear molecule, 10,12-pentacosadiyn-1-ol (PCDO), for constructing the covalent bonding with the GO nanosheets (Figure 7A).[16] The linear PCDO molecules are first grafted with the GO nanosheets through esterification reaction between the alcohol groups at one end of the PCDO and the carboxylic acids on the surface of the GO nanosheets. Different from linear small molecules, the

long chain PCDO molecules can be further cross-linked with each other through 1,4-addition polymerization of their diacetylenic units under UV irradiation.[17] Another intriguing advantage of the PCDO modified GO layered materials is that the cross-linking bonds with the PCDO would simultaneously provide the electron-transfer pathway among the GO nanosheets. The tensile strength is increased to 106.6 ± 17.1 MPa from 95.4 ± 3.9 MPa for as-received GO paper, which is comparable to that of the natural nacre, while the tensile toughness is raised to 2.52 ± 0.59 MJ/m^3, which is 40% higher than that of the natural nacre (∼1.8 MJ/m^3). After reduction of the GO nanosheets, the tensile strength and the toughness of these bioinspired layered materials are improved to 129.6 ± 18.5 MPa and 3.91 ± 0.03 MJ/m^3, respectively. More impressively, the maximum value of the tensile strength is up to 156.8 MPa, and the toughness is two times higher than that of the natural nacre. Detailed observation on the fracture morphology of the PCDO-GO layered materials discloses the origin of improvement in the mechanical properties after PCDO cross-linking (Figure 7B). It is clear that many GO nanosheets are pulled out owing to the strong interactions between the adjacent GO nanosheets and the PCDO molecules. The edges of the GO nanosheets are curved, further demonstrating that breakage of the covalent bonds between the PCDO and the GO nanosheets could cost more energy for fracture and bring obvious deformation of the GO nanosheets. After reduction of the inside GO sheets, the bioinspired layered materials exhibit the identical fracture morphology, and the edges of the reduced GO sheets show even more strongly curved. The whole fracture process of the bioinspired layered materials is illustrated in Figure 7C. The linear PCDO molecules are grafted on the reduced GO nanosheets via the covalent ester bonds, meanwhile the PCDO molecules form the
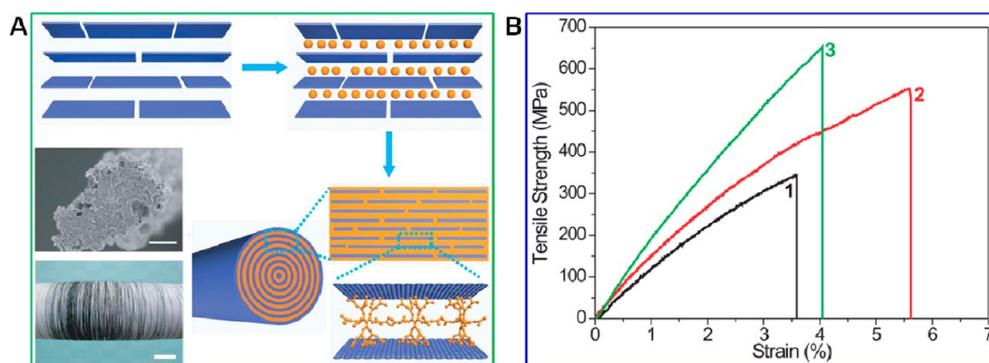
Figure 8. Branched polymer for chemical bonding interface in the layered GO fiber. (A) Scheme of liquid crystal self-templating (LCST) strategy and the resultant bioinspired layered fibers with the hierarchical structures. (B) Typical stress−strain curves for neat GO (1), GO/HPG (2), and GO/HPG-GA (3) fibers (top picture). Reprinted by permission from Macmillan Publishers Ltd: *Sci. Rep.* (ref 22), copyright 2012.
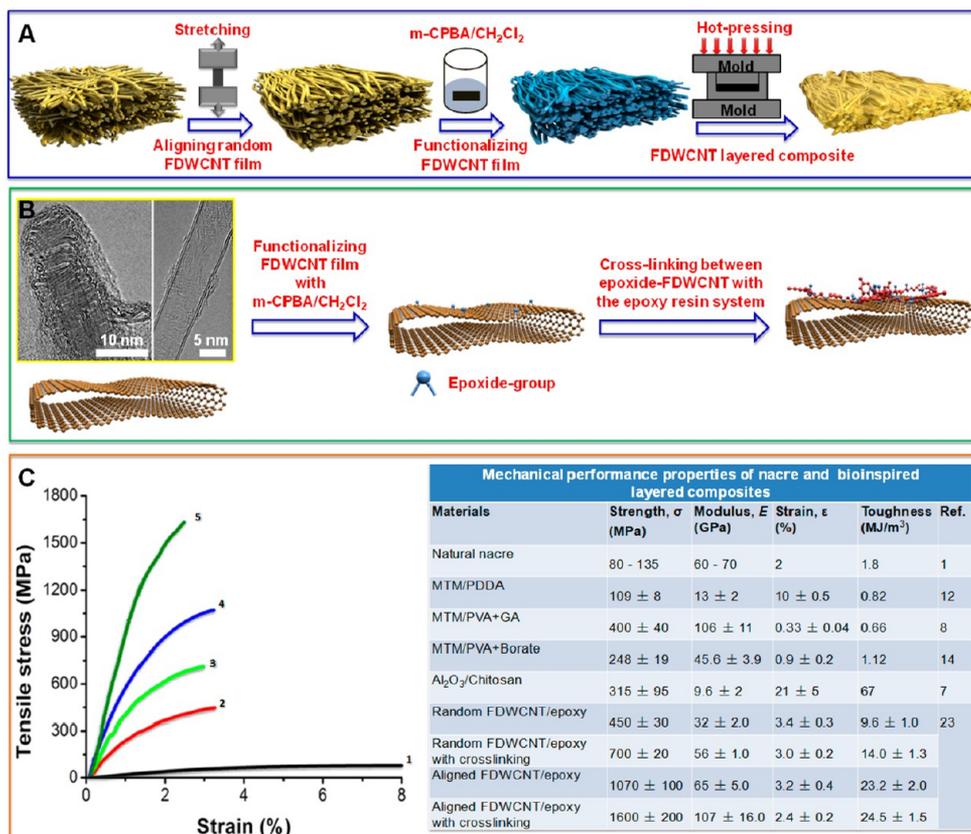
Figure 9. 3D network for covalent bonding. (A) Scheme of fabrication of the flattened double-walled carbon nanotubes (FDWCNTs)/epoxy bioinspired layered materials. (B) Epoxide groups on the FDWCNTs, which are cross-linked with the epoxy matrix in chemical bonds into the 3D network. (C) Mechanical properties of FDWCNTs/epoxy layered materials. Stress−strain curves 1, 2, 3, 4, and 5 represent pure epoxy, random FDWCNT/epoxy, random FDWCNT/epoxy with cross-linking, aligned FDWCNT/epoxy, and aligned FDWCNT/epoxy with cross-linking, respectively. The right table compares mechanical properties of FDWCNTs/epoxy nanocomposites with other bioinspired layered materials. Reprinted with permission from ref 23. Copyright 2012 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

intercross-linked networks through conjugation of ene-yne backbones and adopt a randomly coiled conformation. When loading, the reduced GO nanosheets extensively slide against each other. The weak hydrogen bonds are first ruptured and the coiled PCDO molecules are stretched along the sliding direction, resulting in dissipation of a large amount of energy. When further increasing the loading force, the chemical bonds between the PCDO molecules and the reduced GO nanosheets, as well as the ene-yne backbones in the conjugated

PCDO molecules, are broken, simultaneously resulting in curving of the reduced GO nanosheets.

Compared with the linear molecules, the covalent bonding between the linear polymers and the building blocks would facilitate improving the interfacial strength. Park et al. developed an approach for introducing the covalent bonding between the polyallylamine (PAA) polymers and the GO nanosheets.[18] PAA has a long alkyl chain with a number of reactive amine groups. The oxygen-containing functional groups of the GO nanosheets including epoxy and carboxylic

acid easily react with the amine groups of the PAA polymers, resulting in 30% increase of Young's modulus and 10% increase of tensile strength. Although the experimental results of XPS and FT-IR spectra suggest that the covalent cross-linking happens between GO nanosheets and PAA polymers, the chemical structure of cross-linked GO nanosheets and reaction mechanism remains to be not fully explored yet. Podsiadlo et al. successfully covalently linked the PVA polymers and the nanoclay through the glutaraldehyde (GA).[8] The tensile strength is increased from 150 ± 40 MPa to 400 ± 40 MPa, and the Young's modulus is enhanced from 13 ± 2 GPa to 106 ± 11 GPa, respectively, which is comparable to the mechanical performance of Kevlar fiber.[19] Tian et al. demonstrated the ultrahigh modulus and the high strength of the bioinspired layered materials through covalent bonding between the polydopamine (PDA) modified GO nanosheets and the polyetherimide (PEI) polymers.[20] The covalent bonding is formed between the PEI and the PDA on the surface of the GO nanosheets. The Young's modulus reaches 103.4 GPa, and the tensile strength is as high as 209.9 MPa.

3.3.2. Branched Polymer. The branched polymers have multiple sites that could be potentially used for covalent linking with the building blocks in the layered materials. The hydperbranched polyglycerol (HPG) with abundant functional groups was selected as the elastic glue to construct the bioinspired layered fiber (artificial nacre fibers, Figure 8A) with the GO nanosheets by Hu et al.[21,22] Although the hydrogen bonds work well in the GO-HPG artificial nacre fiber, the covalent bonding is found to be more efficient to improve the mechanical properties. After formation of the covalent acetal bridges between the hydroxyl groups of the HPG polymers and the GO nanosheets, the tensile strength of the layered materials is improved to 652 MPa from 555 MPa and the toughness still keeps about 14 MJ/m^3 (Figure 8B). Compared with conventional engineering metallic alloys, the covalently linked artificial fiber exhibits superior mechanical performance, especially for the specific strength ($\sim$555 N·m/g) due to its lightweight nature (density of $\sim$1 g/cm^3). Thus, the bioinspired layered fiber materials offer a novel type of nanocomposite to exceed the mechanical properties of the natural materials.

3.3.3. Three Dimensional (3D) Network. Regardless of the linear molecules, the linear polymers, or the branched polymers, the chemical bonding is normally formed in the 2D planes. Due to the feature of the thermosetting matrix, such as epoxy resin, the precursors may react to form the 3D network. Thus, one would speculate whether the covalent bonding between the 3D network and the building blocks could dramatically improve the mechanical properties of the layered materials. We successfully constructed the high strength layered materials through covalent bonding in the 3D network.[23] The synthesized multilayered flattened double-walled carbon nanotubes (FDWCNTs) are chosen as the building blocks and assembled into the flexible thin films. These flexible FDWCNT films can be further aligned by simply stretching. The porous FDWCNT scaffolds are easily impregnated by epoxy/acetone solution and pressed into layered materials, and the whole process is shown in Figure 9A. In the curing process of the epoxy resin, the epoxide groups grafted on the FDWCNTs films react with the epoxy constituents, resulting in cross-linking between FDWCNTs and the epoxy matrix (Figure 9B). For the random FDWCNT-epoxy layered materials, the tensile strength and Young's modulus are increased from 450 ± 30 MPa to 700 ± 20 MPa and from 32 ± 2.0 GPa to 56 ± 1.0

GPa, respectively, after covalent cross-linking (Figure 9C). Meanwhile, the toughness is improved from 9.6 ± 1.0 MJ/m^3 to 14.0 ± 1.3 MJ/m^3, which is comparable to that of the GA cross-linked artificial fibers composed of the branched polymer and the GO nanosheets.[22] When the aligned FDWCNTs are used, the tensile strength and Young's modulus of the 3D cross-linked layered composites are further enhanced to 1.6 ± 0.2 GPa and 107 ± 16.0 GPa, respectively. This mechanical strength represents the best result of the reported bioinspired layered materials so far. Correspondingly, the tensile toughness reaches 24.5 ± 1.5 MJ/m^3, which is roughly one order magnitude higher than that of the natural nacre and 36% higher than that of the artificial nacre fibers.[22] Evidently, the 3D covalent cross-linking between FDWCNTs and the epoxy network plays a key role in improving the mechanical properties of the bioinspired layered materials.

As described in part 3.3.1, the ultratough artificial nacre is synthesized by utilizing the concept by grafting the long chain linear molecules on the wedge of the GO nanosheets.[16] As comparison, the brittle nature of the epoxy into the 3D network makes the toughness of the synthesized layered materials not exceptionally high. Though the maximum tensile strength and Young's modulus of the FDWCNT-epoxy layered composites are as high as 1.8 and 123 GPa, respectively, and the toughness is still little lower than that of the Al$_2$O$_3$-chitosan layered materials.[7]

It needs to be mentioned that, in real samples, the outstanding mechanical properties of the resultant layered materials usually originate from combination of multiple interface interactions, which could result in preferable sharing of the load and avoid the stress concentration under the successive failure mode. For example, Kotov et al. reproduced a series of layered nanocomposites by integrating different interface design methods, such as combination of hydrogen and covalent bonding,[8] or linking of hydrogen and ionic bonding.[24] As for nanoclay/PVA nanocomposites,[8] combination of hydrogen bonding and covalent bonding of Al−O−C between nanocaly platelets and PVA chains led to 50% improvement of tensile strength compared with the nanoclay/PDDA with only ionic bonding.[12] Further cross-linking by glutaraldehyde (GA) induced formation of more covalent acetal bridges between nanocaly and PVA, giving rise to extensively efficient load transfer between nanoclay and PVA. Thus, the ultrahigh mechanical properties with tensile strength of 400 MPa and Young's modulus of 106 GPa were achieved. In addition, combination of hydrogen and ionic bonding was also implemented at the interface between nanocaly and PVA in the layered nanocomposites.[24] The hydrogen bonding was explored to be broken and reformed when the PVA and nanoclay platelets slid against each other, showing the sawtooth like stress−strain curve to dissipate the interfacial energy. Further incorporation of Cu^{2+} ions endowed additional ionic bonding at the interface between PVA and clay, causing the dramatic enhancement of the tensile strength and Young's modulus from 150 to 320 MPa and 13 to 60 GPa, respectively.

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
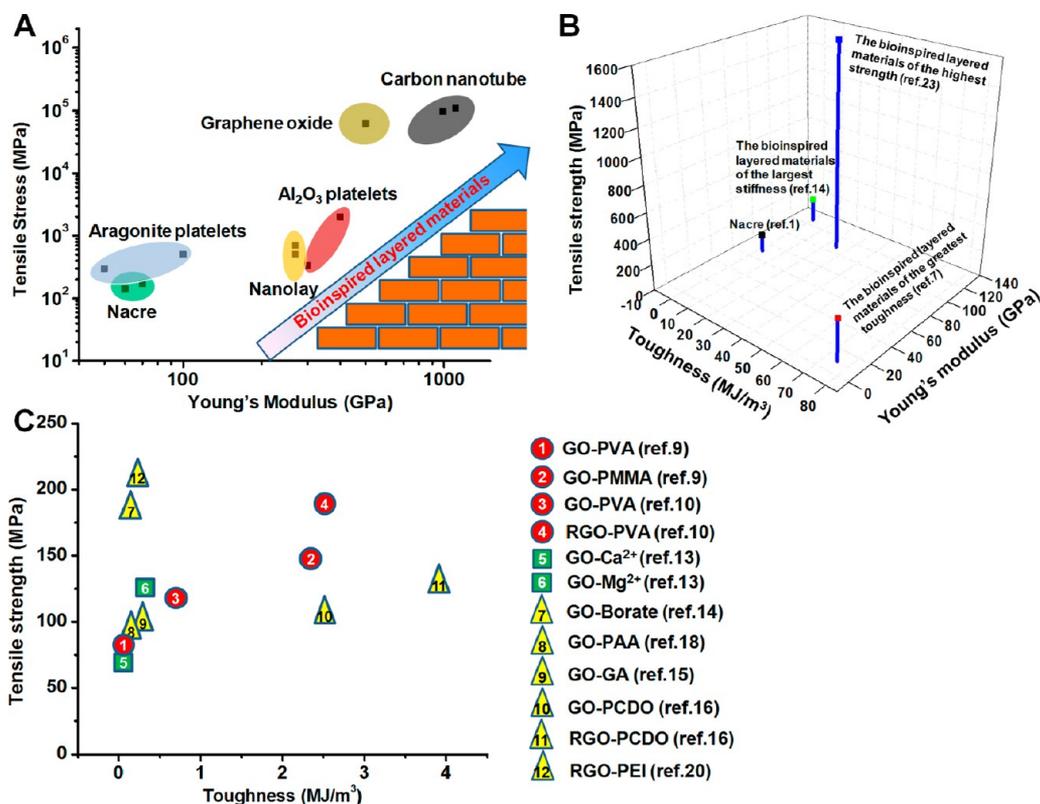
Figure 10. Mechanical properties comparison of intrinsic building blocks and their bioinspired layered materials. (A) Typical building blocks. (B) Reprehensive bioinspired layered materials of prominent mechanical performance. (C) GO-based layered materials with different interface bonding. Red cycles stand for hydrogen bonding, green squares represent ionic bonding, and yellow triangles symbolize covalent bonding.

recent reports, the intrinsic mechanical properties of the building blocks and their bioinspired layered materials are summarized in Figure 10. Several typical building blocks, including man-made $CaCO_3$ platelet,[25] Al_2O_3 flake,[7] nanoclay,[8] CNTs,[23] and GO nanosheet,[16] are compared in mechanical properties (Figure 10A). The aragonite platelets in the natural nacre have a rather low mechanical property with the tensile strength of 334−505 MPa[7,26] and the Young's modulus of 50−100 GPa,[27,28] respectively. As comparison, the 2D nanoclay possesses the high tensile strength of 500−700 MPa[29] and the Young's modulus of about 270 GPa.[30] By using nanoclay as the building blocks, Kotov et al. has demonstrated that the mechanical properties of the clay-PVA bioinspired 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.[8] Another typical 2D building block, Al_2O_3 platelet, also has the outstanding mechanic strength including the tensile strength of 330−2000 MPa[7,31] and the Young's modulus of 300−400 GPa.[7,31] Based on the Al_2O_3 platelets, Studart et al. fabricated the bioinspired layered materials with the record-high toughness of 75 MJ/m^3 so far.[7] Ritchie et al. obtained the ultratough layered materials based on Al_2O_3 platelets with the toughness of 30 MPa·m$^{1/2}$,[31] which is 300 times higher than that of the Al_2O_3 platelets and 10 times higher than that of the natural nacre. 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 and 500 GPa, respectively;[32] 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.[33] Accordingly, we have successfully constructed the bioinspired layered materials of the highest tensile strength based on the CNTs[23] as well as the ultratough layered materials based on the GO sheets.[16] The maximum tensile strength is up to 1800 MPa, which is one magnitude higher than that of the natural nacre (Figure 10B). Meanwhile, the Young's modulus is as high as 123 GPa, almost two times higher than that of the nacre. Obviously, the building blocks of the excellent mechanic strength such as carbon-based nanomaterials should be ideal artificial platelets for fabricating the high performance bioinspired layered materials, even though having the less-elaborate micro/nanoscale structures with respect to the natural layered structures.[7]

Beside selection of the building blocks, the interface design is another key to acquire the layered materials of high mechanical property. To better understand the role of the interface, the detailed mechanical comparison of the layered materials based on the same building blocks (2D GO sheets) is made (Figure 10C). The tensile strength and toughness of GO-based layered materials with hydrogen bonding (red circles) can be perfectly combined due to the adaptive nature of hydrogen bonding (breaking and reforming) during the fracture process. Quite different from the hydrogen bonding, the layered materials with ionic bonding (green squares) show much lower toughness, which is understood that stronger bonds between GO nanosheets result in brittle fracture. Interestingly, among those three types of interface interactions, the covalent bonding (yellow triangles) exhibits much better designability. For instance, the high-strength GO-based layered materials is obtained by covalent bonding with strong polymer of PEI (yellow triangle No. 12),[20] while the very tough GO-based

1264

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layered materials is achieved by covalent bonding with long and flexible PCDO molecules (yellow triangle No. 11).[16] Furthermore, when GO-based layered films covalently bonded with branched polymer of HPG are wrapped into the fibers, both the remarkable tensile strength of 652 MPa and the super toughness of 14 MJ/m^3 are successfully acquired.[22] It should be noted that, with respect to the above-mentioned layered films in Figure 10C, the outstanding mechanical performance of the GO-based layered fibers with the diameters of several micrometers should originate from their defect-free structures, Nevertheless, to apply the covalent bonding at the layered interfaces would be effective way to improve the mechanical performance of the resultant materials. Evidently, the unprecedented mechanical properties of the bioinspired layered materials will be expected to be obtained through replicating the elaborate micro/nanostructure of natural materials by selecting strong building blocks and adopting the suitable interface design in the future.

5. CONCLUSION AND OUTLOOK

This Account reviews recent progress on the interface design of the bioinspired 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 detail. Thanks to understanding and applying the interface design, many novel bioinspired layered materials of high strength, toughness, and stiffness have been constructed, making these artificial materials much more possible for practical application in many fields.

Finally, we suggest that a future development on the bioinspired layered materials is to integrate multiple types of the functional building blocks into the same materials, and the unprecedented mechanic performance can be anticipated to be achieved by taking advantage of the synergistic effects. For instance, we have demonstrated the synergistic toughening effect in the artificial nacre of nanoclay/nanofibrillar cellulose/poly(vinyl alcohol) nanocomposites.[34] The new type of ternary artificial nacre realizes integration of high tensile strength, good toughness, and long fatigue life, superior to natural nacre and other conventional layered nanocaly/polymer binary nanocomposites. Two or more building blocks introduced together into the layered materials with strong interface design will offer new opportunities for obtaining the high performance artificial materials.

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