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Bioinspired Graphene-Based Nanocomposites and Their Application in Flexible Energy Devices

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Graphene is the strongest and stiffest material ever identified and the best electrical conductor known to date, making it an ideal candidate for constructing nanocomposites used in flexible energy devices. However, it remains a great challenge to assemble graphene nanosheets into macrosized high-performance nanocomposites in practical applications of flexible energy devices using traditional approaches. Nacre, the gold standard for biomimicry, provides an excellent example and guideline for assembling twodimensional nanosheets into high-performance nanocomposites. This review summarizes recent research on the bioinspired graphene-based nanocomposites (BGBNs), and discusses different bioinspired assembly strategies for constructing integrated high-strength and -toughness graphene-based nanocomposites through various synergistic effects. Fundamental properties of graphene-based nanocomposites, such as strength, toughness, and electrical conductivities, are highlighted. Applications of the BGBNs in flexible energy devices, as well as potential challenges, are addressed. Inspired from the past work done by the community a roadmap for the future of the BGBNs in flexible energy device applications is depicted.

1. Introduction

Recently, miniaturized portable, and wearable energy devices, have revolutionized our daily life, including electronic papers, touch screens, roll-up displays, and wearable sensors. In order to sustain their use under repetitive loads, flexible configuration is a prerequisite that should be able to convert and/or store energy on repetitive bending, folding or stretching without sacrificing their performance.^[1] Graphene, with extraordinary properties, is the strongest and stiffest material ever identified and the best electrical conductor known to date, which totally satisfies these requirements.^[2] Without a doubt, graphenebased nanocomposites are an ideal candidate. There have been several attempts to use graphene-based nanocomposites in flexible energy devices.^[1,3] However, their assembly using traditional approaches,^[4] exhibit rather poor mechanical and electrical properties, largely limiting the efficiency of these

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devices. It thus remains a great challenge to assemble micro-scale graphene nanosheets into macro-sized high-perfor-

mance nanocomposites. Since 2010, many reviews were published on the graphene-based nanocomposites and their application in energy devices. Wang et al.^[1] focused on applications of flexible graphene energy devices, such as photovoltaic devices, fuel cells, supercapacitors, and batteries. Mao et al.[3] also reviewed various graphenebased materials for flexible electrochemical energy storage devices. Zhou et al.^[5] reviewed recent flexible lithium-ion batteries based on graphene, with special emphasis on the selection of electrode materials and configuration design. Xu et al.^[6] summarized the recent progress in graphene-based electrodes for electrochemical energy storage. Zhu et al.^[7] and Huang et al.^[8] reviewed the graphene and graphene-based materials as alternative

electrode materials for electrochemical energy storage systems, i.e., batteries and supercapacitors. Luo et al.^[9] reviewed the recent progress on preparing the well-defined graphene-based nanomaterials through chemical and thermal approaches and their applications in energy-related areas. Weiss et al.^[10] summarized the fabrication of graphene, their physical properties and applications in electronic devices. Sahoo et al.[11] summarized and compared the advancement of graphene-based materials for energy conversion devices in fuel cells and solar cells applications. Wan et al.^[12] summarized graphene applications in organic photovoltaic (OPV) cells, containing transparent electrodes, active layers and interfaces layer in OPV. Pang et al.^[13] gave a brief summary on the synthesis of graphene and applications in organic electronics. Eda et al.^[14] reviewed the fundamental structure and properties of chemically derived graphene oxide and discussed their potential applications in electronics and optoelectronics. Shao et al.^[15] reviewed the recent progress in interfacial self-assembly techniques for graphene oxide films, including liquid-air, liquid-liquid and liquid-solid interfaces.

The above mentioned reviews are focused on the applications of graphene-based nanocomposites in flexible energy devices. The performance of nanocomposites is usually dictated by their unique structure and architecture. How to achieve the high-performance flexible energy device through designing and constructing optimal structures of graphene-based nanocomposites is not obvious. It is critical to develop new fabrication



techniques that are able to make these materials in bulk form. Living organisms are one place to seek inspiration for making something new and original. Nacre, the 'gold standard' for biomimicry having both high strength and toughness, has been the source of inspiration for designing many synthetic hybrid materials and nanocomposites.^[16–20] Nacre achieves this through a precise architecture that resembles that of a brick wall, and clever design of the interfaces. Compared to other approaches for constructing graphene-based nanocomposites,^[4,21] this bioinspired concept results in good dispersion, high loading and excellent interfacial interaction design. The resultant bioinspired graphene-based nanocomposites (BGBNs) demonstrate significant enhancement in mechanical and electrical properties.^[22]

In this review, we summarize recent achievements on BGBNs, for example, discussing the assembly approaches, comparing the different interfacial interactions, and revealing the synergistic effects therein. We highlight the fundamental properties of BGBNs, such as strength, toughness, and electrical conductivity. Then, we also summarize applications of the BGBNs in flexible energy devices, and discuss their challenges. Finally, we offer a perspective on how to construct integrated strong and tough BGBNs through the synergistic effects from interfacial interactions and building blocks, providing some inspiration to the community and a clear vision for the future in the application of flexible energy devices.

1.1. Inspiration from Nature

Nacre shows an ordered layered structure,^[16,23-25] as shown in Figure 1A. It is a typical brick-and-mortar structure, with bricks composed of inorganic CaCO3 mineral platelets (aragonite) and mortar of organic layer. The mineral platelets are comprised of millions of nanograins (≈30 nm), and the organic layer contain acidic proteins and a chitin network. This hierarchical micro-/nanoscale inorganic-organic structure results in the nacre's outstanding mechanical properties, especially its fracture toughness, which is almost three orders of magnitude higher than that of monolithic calcium carbonate. Nacre's properties are far in excess of those of their constituents, by violating the "law of mixtures" as shown in Figure 1B. When the crack propagates in nacre, as shown in Figure 1C, the path is deflected around the orderly lavered structure, leading to much more effective energy dissipation than a straight crack path. In this process, the abundant interfaces play a key role in deflecting crack propagation. Several types of toughening mechanisms between alternatively ordered CaCO₃ platelets have been categorized as follows: mineral bridges between CaCO3 platelets; nano-asperities for shearing resistance; organic glue; and tablet interlocking, as shown in Figure 1D.

The inspiration from nacre is that the orderly hierarchical micro-/nanoscale structure and effective interfacial interactions between inorganic and organic components play a key role in promoting exceptional mechanical properties. Several inorganic building blocks have been used to successfully mimic nacre-like composites, such as man-made calcium carbonate (CaCO₃) platelet,^[26,27] aluminum oxide (Al₂O₃) flake,^[28] montmorillonite





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(MTM),^[19,29–36] hydroxyapatite (HA),^[37,38] acrylonitrile butadiene styrene (ABS),^[39] and carbon nanotubes (CNTs).^[40] Employing these building blocks, the fabricated bioinspired composites showed excellent mechanical properties. Readers can refer to previous reviews for the comparison between these bioinspired composites.^[17–20,25]

Recently, two dimensional (2D) graphene or graphene oxide (GO) have attracted much research interest owing to their outstanding mechanical and electrical properties.^[2,41,42] Because GO nanosheets have many functional oxygen-containing groups on their surface, different interfacial interactions can be constructed with the second component in the BGBNs. Thus GO nanosheets are one of the best candidates for fabricating bioinspired nacre-mimetic nanocomposites.



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Figure 1. Hierarchical structure and interfacial interactions in natural nacre. (A) The ordered layered structure of nacre with inorganic CaCO₃ platelets and organic layer, containing biopolymer and fibrous chitin network. (B) Nacre display a toughness that is orders of magnitude higher than either the aragonite or biopolymer layer, clearly violating the "rule of mixtures". (C) Cracks in natural nacre are deflected around the ordered layered structure, thus dissipating more energy (yellow arrows show the direction of tension). (D) The micro-scale aragonite platelets promote four kinds of interfacial interactions: (i) mineral bridges between CaCO₃ platelets; (ii) nano-asperities for shearing resistance; (iii) organic glue; and (iv) tablet interlocking. Reproduced with permission.^[16] Copyright 2014, Nature Publishing Group.

1.2. Extraordinary Properties of Graphene

Since the experimental successful exfoliation of high-quality single layer graphene in 2004,^[43] this novel two-dimensional (2D) carbon nanomaterial has attracted a great deal of attention from both academia and industry. The pure sp² hybridization network of graphene results in its extraordinary physical properties. Lee et al.^[44] demonstrated the elastic properties and intrinsic breaking strength of free-standing graphene monolayer through nano-indentation with an atomic force microscope (AFM). As shown in **Figure 2**A, the graphene monolayer flakes were first mechanically deposited onto the substrate

with many circular wells. The graphene membranes were stretched tautly across the well openings through the van der Waals attraction to the substrate, as shown in Figure 2B. Then the mechanical properties of the graphene monolayer were probed through indenting the center of each monolayer graphene with an AFM, as shown in Figure 2C. In the process of mechanical testing, a constant displacement rate was applied to repeat the cycle several times until hysteresis was no longer observed, indicating that the monolayer graphene film did not slip around the periphery of the well. Once the data for the elastic properties were recorded, the graphene film was once again indented at the same rate, demonstrating the failure of

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Figure 2. Mechanical properties of monolayer graphene. (A) SEM image of the monolayer graphene spanningan array of circularholes. Area I shows a hole partially coveredby the graphene, area II is fully covered, and area III was fractured during indentation (scale bar, 3 mm). (B) Noncontact mode AFM image of one monolayer, 1.5 mm in diameter. (C) Schematic of the nanoindentation on suspended monolayer graphene. (D) AFM image of the fractured graphene monolayer. (E) Comparison of the stress–strain curves of graphene monolayer: red dashed line represents the experimental results, and the blue curve shows the simulation results. Reproduced with permission.^[44] Copyright 2008, American Association for the Advancement of Science.

the graphene film, as shown in Figure 2D. The mechanical properties including elastic modulus and breaking stress of the graphene monolayer were calculated through processing force-displacement data, as shown in Figure 2E. The Young's modulus and the strength of the monolayer are about 1.0 ± 0.1 TPa, and 130 ± 10 GPa, respectively, with high strain of 25%, consistent with the simulation prediction.^[45] These mechanical properties of graphene are higher than those reported for carbon nanotubes (CNTs).^[46,47]

Graphene also shows high electrical conductivity, as high as 6×10^3 S cm⁻¹,^[48] resulting in its numerous promising applications in many fields, such as aerospace, flexible supercapacitor electrodes, smart and intelligent devices. Generally, there are two ways to obtain graphene materials.^[2] One is the bottom-up approach of chemical vapor deposition. The resultant graphene film shows high intrinsic physical properties. However, this technique is time consuming and difficult to produce a large amount of graphene film. The other is the top-down approach of mechanical exfoliation that is equally difficult to obtain a large amount of graphene film for practical applications. Chemical exfoliation of graphite flakes is the usual method (Hummers' method), in which the graphite flakes are heavily oxygenated into graphene oxide (GO) nanosheets. GO nanosheets possess abundant functional groups such as hydroxyl, epoxide functional groups on their basal planes, and carboxyl groups located at their edges, which facilitates the interface design for constructing BGBNs.

2. Bioinspired Graphene-Based Nanocomposites

Inspired by the orderly hierarchical micro-/nanoscale structure and abundant interfacial interactions of nacre, a series of BGBNs have been demonstrated.^[17,22] The bioinspired concept successfully solves the major problems of the graphene-based nanocomposites: poor dispersion, low loading of graphene and weak interface between graphene and polymer matrix. The bioinspired strategy for graphene-based nanocomposites is illustrated in Figure 3. First, the unique structure of nacre is described and characterized. Then, based on the GO nanosheets, the bioinspired strategies are developed to fabricate graphene-based nanocomposites. In binary BGBNs, interfacial interactions play a key role in enhancing the mechanical and electrical properties, mainly including hydrogen bonding, ionic bonding, π - π interactions, and covalent bonding. Furthermore, synergistic effects can be built based on these interfacial interactions to adjust the mechanical properties of resultant BGBNs. As an example, an attempt has been made to combine two kinds of interfacial interactions together in recent reports. In this way, the integrated high strength and toughness of BGBNs have been successfully achieved. In addition, the new ternary BGBNs were created, and the new functions were achieved through introducing the second functional building blocks, such as fatigue property, fire retardant property, etc. Based on this research approach, multifunctional integrated graphene-based nanocomposites will be achieved soon.

2.1. Assembly Approaches

Typical traditional methods for preparing graphene-based nanocomposites,^[4] including liquid mixing, melt mixing, mechanical blending and in-situ polymerization, usually result in low loading, and poor dispersion of graphene in the matrix. Thus, the resultant graphene-based nanocomposites show low mechanical and electrical properties. For example, Stankovich et al.^[49] demonstrated graphene-polystyrene nanocomposites through the addition of polystyrene to the phenyl isocyanate-treated GO dispersion with assisted stirring. Although the obtained graphene-based nanocomposites show electrical conductivity of 0.1 S cm⁻¹ at only 1 vol.% of graphene with good dispersion, the maximum volume fraction of graphene only reaches 2.4 vol.% by this method. Thus, the intrinsic

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Bioinspired Strategy for Graphene-based Nanocomposites



Invention



Binary bioinspired graphene-based nanocomposites *via* interface interactions

Creation



Ternary bioinspired graphene-based nanocomposites through synergistic toughening

		4	Br.B	X	vvv.	(AMB)	MOVOR	-
Graphene	Hydrogen	lonic	Conjugated	Branched	Linear molecule	3D	2D	Nanofiber
	bond	bond	molecule	polymer	and polymer	network	nanosheets	

Figure 3. Bioinspired strategy for creation, assembly fabrication of graphene-based nanocomposites. Nacre shows extraordinary toughness, attributed to its hierarchical micro-/nanoscale structure and abundant interfacial interactions. Nacre provides an inspiration for constructing graphene-based nanocomposites through interfacial interactions, including hydrogen, ionic, and covalent bonding plus π - π interactions. The 1D bioinspired ultra strong graphene-based fiber and 2D bioinspired ultratough nanocomposites have been fabricated through interfacial interactions. The ternary bioinspired graphene-based nanocomposites were also fabricated through synergistic toughening using 1D nanofibrils, and 2D nanoplatetes with graphene nanosheets. In addition to excellent static mechanical properties, other functions have been also developed, such as excellent fatigue, fire-retardant, and many others.

mechanical strength and electrical conductivity of graphene nanosheets are very difficult to be realized in this approach.

Until now, several representative approaches for preparing BGBNs have been developed, as shown in **Figure 4**, including layer-by-layer (LBL), filtration, evaporation, electrophoretic deposition, hydrogel casting, and freeze casting. These assembly approaches have their own characteristics for constructing the BGBNs, and will be presented and discussed in detail as following.

2.1.1. Layer-by-Layer

Layer-by-layer (LBL) assembly,^[50,51] a prevalent approach for coating functional thin films on the substrates, is a cyclical process for fabricating nanocomposites, as shown in Figure 4A.

One cyclical process contains three steps: first, a charged component is adsorbed onto a substrate; second, the substrate needs to be washed before absorbing the second component; third, an oppositely charged component is adsorbed on top of the first layer. This one cyclical process results in a single bilayer with nanometer-scale thickness, and then the deposition process is further repeated until the desired thickness of multilayer film is achieved. Based on processing techniques, the LBL assembly technology can be categorized into: immersive, spin, spray, electromagnetic, and fluidic assemblies. Compared to aforementioned assembly approaches, the LBL assembly allows for precise control of thickness of one component laver in the composites. The simplicity, versatility, and nanoscale control of LBL assembly makes it one of the most widely used techniques for coating both planar and particulate substrates in many fields, such as optics, energy, separation, and for fabrication of nanocomposites. For example, Podsiadlo et al.^[34] demonstrated the fabrication of bioinspired nanoclay-PVA layered nanocomposites with Young's modulus of 107 GPa through immersive LBL approach. Studart et al.^[28] fabricated the highest toughness bioinspired Al₂O₃-PMMA with toughness of 75 MJ m⁻³ via spin LBL technique. BGBNs have been prepared using LBL technique, while molecular interfacial interactions, such as hydrogen bonding, covalent bonding and π - π interactions are easily introduced into the LBL process, resulting in high performance of products.^[52,53] For example, Kotov et al.^[54] prepared an ultrathin selfassembled graphite oxide/polyelectrolytes conductive film via sequential LBL assembly followed by subsequent in situ reduction, which shows a unique chemical stability to concentrated acid or basic solutions and

resistance to photodegradation. Fendler et al.^[55] assembled poly(diallyldimethyl-ammonium) chloride, graphite oxide nanoplatelets, polyethylene oxide into cationic working electrodes via LBL assembly with high specific capacities. Xiong et al.^[56] constructed graphene/diazonium nanocomposite via LBL assembly followed by covalent photo-cross-linking, which shows excellent electrochemical stability in aqueous and organic solutions. Yu et al.^[57] demonstrated graphene/ carbon nanotube bioinspired nanocomposite prepared via LBL assembly with well-defined nanopores structure, which exhibits a nearly rectangular cyclic voltammogram to be promising candidate for supercapacitor electrodes.

For example, Hu et al.^[52] demonstrated high-performance bioinspired nanocomposites based on GO and silk fibroin (SL) through LBL technique. SL molecule chains with numerous functional groups can easily form interfacial interactions





Figure 4. Representative approaches for constructing bioinspired graphene-based nanocomposites. (A) layer-by-layer (LBL). Reproduced with permission.^[50] Copyright 2015, American Association for the Advancement of Science. (B) Filtration. Reproduced with permission.^[58] Copyright 2013, American Chemical Society. (C) Evaporation. Reproduced with permission.^[62] Copyright 2014, American Chemical Society. (D) Electrophoretic deposition. Reproduced with permission.^[63] Copyright 2013, American Chemical Society. (E) Hydrogel casting. Reproduced with permission.^[64] Copyright 2015, Wiley-VCH. (F) Freeze casting. Reproduced with permission.^[16] Copyright 2014, Nature Publishing Group.

with GO sheets, such as hydrogen bonding, polar-polar, and hydrophobic-hydrophobic interactions. The resultant GO-SL nanocomposites exhibit outstanding mechanical properties: tensile strength of more than 300 MPa, Young's modulus of 145 GPa, and a toughness above 2.2 MJ m⁻³. On the other hand, the molecular interphase zones are formed, which are facilitated through dense network of synergistic interfacial interactions between GO sheets and SL domains with intimate contact of 5 nm-thick bilayer. Thus, a much more efficient reinforcing effect is achieved, resulting in record high mechanical properties. Recently, Xiong et al.^[53] successfully demonstrated the ultrastiff BGBNs through assembling GO nanosheets and cellulose nanocrystals via LBL technique, and the elastic modulus reaches a record of 169 GPa, which will be discussed in the following section.

Zhu, et al.^[58] systematically investigated the relative advantages and disadvantages of LBL versus vacuum-assisted filtration (VAF) for assembling bioinspired rGO-PVA nanocomposites. Structures, mechanical and electrical properties were evaluated side by side. The experimental results show clear differences at atomic and nanoscale structural levels, but similarities in micrometer and submicrometer organization for both LBL and VAF techniques. For example, the mechanical properties of bioinspired rGO-PVA nanocomposites with high rGO contents are virtually identical for both techniques. As electrical properties are largely determined by the tunneling barrier between rGO nanosheets and are strongly dependent on atomic/nanoscale organization, LBL technique will be superior to VAF in terms of improving the electrical conductivity of BGBNs

2.1.2. Filtration

Filtration is a straightforward, easily operable yet effective method for assembling nanoscale size materials into microsized materials.^[15] As for 2D graphene and GO nanosheets, the orderly layered structure with good alignment is easily obtained through filtration. For example, Dikin, et al.^[59] prepared GO paper through vacuum-assisted filtration. The maximum tensile strength and modulus of resultant GO paper reach up to 133 MPa, and 32 GPa, respectively. In this process, some content of water was also introduced into the interlaminar of GO paper, forming hydrogen bonds with adjacent GO nanosheets and enhancing the mechanical properties of the resultant materials. Lately, many water-solvent, and oleosolvent molecules and polymers such as dopamine (DA), poly (vinyl alcohol) (PVA), chitosan (CS), and poly (methyl methacrylate) (PMMA) were used to construct the BGBNs through filtration method, as shown in Figure 4B. In addition, Qiu et al.^[60] constructed electrochemical reduced GO/CNTs hybrid films by vacuum filtration, which shows more excellent electrochemical properties compared with pure chemically converted graphene (CCG) films. In principle, the filtration method is a facile way for preparing the graphene-based nanocomposites,^[58] however, the sample size is always limited by the



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diameter of filtration flasks, resulting in difficulty of scaling up fabrication of BGBNs.

2.1.3. Evaporation

Compared with filtration, evaporation benefits from being free of the size limit for preparing BGBNs, with additional advantage of being a simple operation,^[61,62] as shown in Figure 4C. In the process of evaporation, the suspension of GO nanosheets and molecules or polymers is required to remain in homogeneous liquid for long time, because the evaporation process usually takes a long time, from tens of hours to several days. Sometimes, the temperature is raised to accelerate evaporation, however, higher temperature may lead to poorly ordered nanostructures. Although the aforementioned two simple assembly methods are easy in terms of operation, GO nanosheets and organic phase orderly structure of resultant BGBNs cannot be precisely controlled. Thus, other assembly approaches need to be explored for preparing the controllable orderly BGBNs.

2.1.4. Electrophoretic Deposition

Electrophoretic deposition (EPD),^[63] a materials processing technique, entails a two-step process: charged particles in suspension are driven toward an electrode of opposite charge due to influence of an electric field, and then deposit to form a compact film, as demonstrated in Figure 4D. EPD is a versatile technique, widely applied in ceramics and colloidal processing and now increasingly for manipulation of graphene. The dispersion of graphene and graphene oxide in organic solvents, and water can be operated through EPD technique. The morphology of the resultant BGBNs can be tuned through deposition time under constant voltage conditions. In addition, graphenebased nanocomposites can be deposited on three-dimensional, porous and flexible substrates besides simple smooth and flat substrates. Electrophoretically deposited BGBNs show excellent properties, such as high electrical conductivity, good thermal stability, and outstanding mechanical properties. Although EPD is a simple, versatile, easily operable processing technique, the size of the nanocomposites prepared in this way is again limited by the electrophoretic instrument.

2.1.5. Hydrogel Casting

GO nanosheets are considered to be 2D amphiphilic polymer with edge-to-center arrangement of hydrophobic and hydrophilic segments, which can be swelled in water and easily self-assembled into network structure.^[64] The relatively lower critical gelation concentration of GO hydrogel can be obtained due to van der Waals interaction or hydrogen bonding via subtly adjusting the hydrophilic/hydrophobic balance. The resultant GO hydrogel shows higher viscosity at low shear rate, and rheological shear-thinning behavior, which afforded the GO hydrogel an excellent processing ability. The other several preparing methods of GO hydrogel are discussed in detail in the previous review.^[65] The viscous GO hydrogel is cast on

REVIEW

flat substrate with a blade into the thin GO film, and dried at ambient temperature into compact GO film. After chemical reduction, the reduced GO film can be easily peeled off from the substrate. The whole process of GO hydrogel casting is shown in Figure 4E. With assistance of various polymers, GO nanosheets can readily self-assemble into composite hydrogel in water.^[66] and then the composite hydrogel was compressed into BGBNs.^[67-75] The size, shape, and thickness of resultant BGBNs depends on the amount of GO hydrogel and the surface area of substrate.

The hydrogel casting technique, has been developed as a general route for fabricating high-performance BGBNs.^[73] The polymer matrix has been extended to commonly used polymers, including PVA, hydroxypropylcellulose (HPC), polyethylenimine (PEI), polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO), polydimethyldiallylammonium chloride (PDDA), chitosan (CS), spermine, and sodium carboxymethylcellulose (CMC), respectively. The resultant BGBNs fabricated through this technique demonstrated higher mechanical properties than the filtration and evaporation process.

For example, Zhang et al.^[70] demonstrated high-performance graphene-based nanocomposites through hydrogel casting. In the fabrication process, the synthesized poly(acrylic acid-co-(4-acrylamidophenyl) boronic acid) (PAPB) was introduced to construct π - π interfacial interactions between adjacent GO nanosheets besides hydrogen bonding. The resultant nanocomposites (rGO-PAPB) show extraordinary mechanical properties with tensile strength of 382 MPa, and toughness of 7.5 MJ m⁻³, as well as high electrical conductivity of 337 S cm⁻¹.

2.1.6. Freeze Casting

Freeze casting, known as ice-templating,^[37,38,76,77] is a new method for mimicking natural nacre over several length scales. It is first used to freeze ceramic-based suspension under conditions shown in Figure 4F. The lamellar ice crystals are formed, expelling ceramic particles as they grow. Then the sublimation of the water results in a layered homogeneous ceramic scaffold. The brick-and-mortar nacre-mimetic structure can be achieved through compressing the layered ceramic scaffolds, and filling with a second soft phase. In addition, the hierarchical micro/ nanoscale structure can also be obtained via controlling the freezing kinetics and the composition of the suspension. Furthermore, the thickness of lamellae can be manipulated by adjusting the freezing speed to as thin as 1 µm, and the roughness of the lamellae can be achieved at micrometer level via adding sucrose, salts, or ethanol. Moreover, the inorganic bridges between lamellae can also be constructed through adjusting the growth of ice crystals. These factors control the sliding of ceramic bricks relative to each other, which is the dominant mechanism to obtain toughness of resultant nacremimetic composites. Many bioinspired layered composites have been fabricated via freeze casting, such as poly (methyl methacrylate) (PMMA)/alumina (Al₂O₃), PMMA/silicon nitride (SiN) hybrid layered composites. Recently, the graphene-based nanocomposites were also demonstrated via freeze casting, showing the excellent mechanical properties.^[78-82] For example, Vickery, et al.^[82] demonstrated bioinspired nanocomposites





based on GO nanosheets and matrix of PVA. The resultant nanocomposites show higher-order 3D architectures such as sponge-like macroporous scaffolds, and are easily scaled up by freeze casting approach.

The aforementioned six types of strategies have been successfully developed to prepare the BGBNs. The comparison of these approaches is listed in **Table 1**, including, advantages and disadvantages for each approach.

2.2. Interface Design

Nacre with micro-/nanoscale hierarchical structure shows large interface between inorganic CaCO3 platelets and protein matrix. Ample interfacial interactions (Figure 1D), such as, mineral bridges between CaCO3 platelets, nano-asperities for shearing resistance, organic glue, and tablet interlocking, play a key role in the extraordinary mechanical properties of nacre. It should be stressed that the intricate architectures, resulting from the size, shape and arrangement of the building blocks over several length scales, namely so-called multiscale effects, are also highly responsible for the unique integration of high strength and toughness of nacre. In this review, much more attentions are yet payed to the effect of interfacial interactions on the mechanical properties. Nacre inspiration provides the possibility of interface design in the BGBNs, especially for GO nanosheets due to their abundant functional groups on the surface and edge. Two typical categories of the interfacial interactions are non-covalent and covalent bonding. The non-covalent

Table 1.	Comparison	of six strategies	for fabricating BGBNs.
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Strategies	Advantages	Disadvantages		
Layer-by-layer	• Precise control of alternative layered structure	• Time-consuming		
	• High loading of graphene phase	• Difficult to scale up		
Infiltration	 Simple, easy operation 	• Difficult to scale up		
	• Well layered structure	• Thickness of film (<10 µm)		
Evaporation	• Easy operation	• GO nanosheets/organic phase orderly structure is dif- ficult to be precisely controlled		
	• Easy to scale up	 Time-consuming 		
Electrophoretic deposition	• Simple for thin film	• Difficult to prepare thick film		
	• Suitable for many kinds of substrates, such as planar, 3D, porous, flexible	• Low mechanical properties of resultant layered composites		
Hydrogel casting	g • Fast, economical, large-scale preparation	• Difficult to control the layered structure		
	• Film layered materials	• Difficult to design interfacial interactions		
	• Easy operation			
Freeze casting	Bulk composites	 Energy-consuming during freezing and sintering 		
	Inexpensive procedure	• Difficult for preparing thin film		
	Brick-and-mortar structure			

bonding contains hydrogen bonding, ionic bonding, and π - π interaction, which are relatively weaker than that of covalent bonding because of chemical reactions in the processing. In addition, more than one type of interfacial interactions operate together in the natural materials providing contribution to the mechanical properties. Thus, the combination of interfacial interactions is also effective strategy for preparing the BGBNs, resulting in the synergistic effect. The synergistic effect can be optimized through combining different interfacial interactions. In the following sections, several representative interfacial interactions will be discussed in detail, and the synergistic effect from interfacial interactions is also discussed and compared to evaluate the optimal synergistic effect for constructing highperformance BGBNs. To make a comparison, the toughness of materials is calculated by area under the tensile stress-strain curves in this review. Apart from the mechanical properties, the electrical conductivity, closely associated with the performances of flexible energy devices, will be also analyzed and compared to provide a comprehensive insight about nacre-inspired interfacial design when fabricating integrated high-performance BGBNs.

2.2.1. Hydrogen Bonding

Hydrogen bonding is easily constructed in the process of preparing the BGBNs. For example, Dikin et al.^[59] first assembled GO paper through abundant hydrogen bonding between adjacent GO nanosheets with water molecules via vacuum-assisted filtration, as shown in Figure 5A. The orderly GO nanosheets structure is clearly observed in the cross-section morphology, as shown in Figure 5B. This kind of GO paper with cross-linking of hydrogen bonding shows high mechanical properties with tensile strength of 133 MPa and Young's modulus of 32 GPa. The bending experiments of GO paper demonstrate more deformation than uniaxial tensile testing. That is because the uniaxial tension leads to an equal distribution of stresses through the shear deformation of the interlamellar hydrogen bonding with water molecules, whereas the bending process introduce highly localized stresses at the surfaces. At the outer surface, the stress results in delamination of layers along the defects in the stacked structure. On the other hand, the stress at the inner surface leads to a local shear and buckling of the GO layers. These experimental results suggest that the GO paper with hydrogen bonding is a stiff in plane but compliant out of plane macroscopic material with tightly interlocked GO nanosheets. In addition, the GO paper is well known to be insulated due to the abundant defects and functional groups on GO surface. Pei et al.^[83] directly reduced the GO film into the highly conductive and flexible reduced GO (rGO) film by hydroiodic (HI) acid, which could effectively remove the defects and partially recover the sp² conjugated structure of graphitic lattice. Compared with GO film, the rGO film not only shows more excellent electrical conductivity of 298 S cm⁻¹, but also possesses much higher tensile strength of 170 MPa and toughness of 2.98 MJ m⁻³ due to the increased π - π stacking interaction and decreased *d*-spacing of adjacent rGO nanosheets, which allows this material to be applied in application of flexible energy devices. Besides of the 2D pure graphene films, the 1D GO or graphene fibers^[84-89]

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Figure 5. Utilization of hydrogen bonding for construction of bioinspired graphene-based nanocomposites. (A) Assembled GO paper. Reproduced with permission.^[59] Copyright 2007, Nature Publishing Group. (B) SEM image of the cross-section morphology of GO paper. Reproduced with permission.^[59] Copyright 2007, Nature Publishing Group. (C) Illustration of hydrogen bonding formed between GO nanosheets with PVA and PMMA chains. Reproduced with permission.^[90] Copyright 2010, Wiley-VCH. (D) The digital photograph of 1D bioinspired graphene-based fiber nanocomposite of GO-HPG. Reproduced with permission.^[90] Copyright 2012, Nature Publishing Group. (E) The proposed hierarchical structure of GO-HPG via wetspinning. Reproduced with permission.^[99] Copyright 2012, Nature Publishing Group. (F) Illustration of the network of hydrogen bonding between adjacent HPG attached to the GO building blocks. Reproduced with permission.^[99] Copyright 2012, Nature Publishing Group. (F) Attached to the GO building blocks. Reproduced with permission.^[99] Copyright 2012, Nature Publishing Group. (F) Illustration of the network of hydrogen bonding between adjacent HPG attached to the GO building blocks. Reproduced with permission.^[99] Copyright 2012, Nature Publishing Group.

also show excellent mechanical properties due to the hydrogen bonding.

Polymers with hydroxyl groups or oxygen groups, such as PVA,^[90,91] CS,^[92,93] HPC,^[66] poly(acrylic acid),^[94] polydopamine (PDA),^[62] poly(N-isopropyl acrylamide) (PNIPAM),^[95] and poly(methyl methacrylate)(PMMA),^[90] are good choices for forming hydrogen bonding with adjacent GO nanosheets in the BGBNs. For example, Putz et al.^[90] compared the effect of hydrogen bonding on the mechanical properties of BGBNs with polymers of PVA and PMMA (designated as GO-PVA, and GO-PMMA). Figure 5C illustrates the formed hydrogen bonding networks between pendant hydroxyl groups of PVA chains with GO nanosheets in GO-PVA nanocomposites, and the ester functional groups on the side chain of PMMA with GO nanosheets in GO-PMMA nanocomposites. The hydroxyl groups on the PVA chain act as both hydrogen bonding acceptors and donors, moreover, the covalent C-C bonds of PVA further link hydrogen bonding into a bridge. Thus the hydrogen bonding network is easily formed in GO-PVA nanocomposites, resulting in much stronger interfacial interactions than water molecules in GO paper. The ample strong hydrogen bonding network and the orderly layered structure of bioinspired GO-PVA nanocomposites achieve higher mechanical properties than that of a simple rule-of-mixtures calculation only with GO and PVA compounds. The storage modulus of bioinspired GO-PVA nanocomposites with 77.4 wt.% GO is two times higher than that of the calculated value from the rule-of-mixtures. Different from PVA, PMMA can only act as a hydrogen bonding acceptor through the ester functional groups on the side chain. The resulted hydrogen bonding in GO-PMMA nanocomposites is limited by the hydrophobicity and steric hindrance of the methyl groups of the methacrylate side chains. Thus, the moduli of GO-PMMA nanocomposites are lower, and only minimally affected by the PMMA content. The resultant moduli of GO-PMMA nanocomposites are close to the value calculated from the rule-of-mixtures.

The reduced GO-PVA (rGO-PVA) nanocomposites with 80 wt% GO demonstrate high tensile strength of 188.9 MPa and toughness of 2.52 MJ m^{-3.[91]} The oxygen-containing groups on the GO nanosheets are mostly removed by hydroiodic acid (HI), and thus the interlayer spacing of rGO-PVA nanocomposites will dramatically decrease, resulting in much stronger interactions of π - π stacking between adjacent GO nanosheets. Other oxygen-containing groups at the edge of GO nanosheets cannot be removed in the process of chemical reduction.^[83] Thus, the hydrogen bonding network still works very well for improving the mechanical properties of resultant bioinspired rGO-PVA nanocomposites. This is the underlying reason why high tensile strength is obtained after chemical reduction. Moreover, while the electrical conductivity (52.65 S cm^{-1}) of the rGO-PVA nanocomposite is four orders of magnitude higher than the corresponding GO-PVA nanocomposite, it is still a little lower compared with the above pure rGO film, which is attributed to the insertion of insulated PVA into rGO. Thus, the hydrogen bonding provided by the insulated polymer is beneficial to the mechanical properties but detrimental to the electrical conductivity of BGBNs.

In order to quantitatively investigate the effect of hydrogen bonding network on the mechanical properties of graphenebased nanocomposites, the molecular dynamic simulations is applied.^[96] In the hydrated GO paper, hydrogen bonding is formed not only between the functional groups on the GO

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nanosheets, but also between GO and water molecules. The simulation results indicate that the hydrogen bonding networks, including oxygen-containing groups on GO nanosheets, as well as water molecules in the interlayer cavities of GO paper, control the mechanical properties of hydrated GO paper. Thus, it is possible to tune the mechanical properties of hydrated GO paper through altering the number of hydrogen bonding networks between GO nanosheets and interlayer water molecules. In addition, the joint experimental-theoretical and computational simulation is introduced to reveal a delicate relationship between the stiffness of GO-PVA nanocomposites and water content.^[97] The synergistic effect of hydrogen bonding network in gallery of GO-PVA nanocomposites can be further enhanced by PVA chain. The stiffness of the GO-PVA nanocomposites is also greatly improved, in a similar fashion found in natural biocomposites, such as spider silk and collagen.^[98] These findings provide guidance for tuning mechanical properties of BGBNs through constructing the hydrogen boning networks.

Xu et al.^[99] demonstrated the multifunctional 1D bioinspired graphene-based fiber nanocomposites, as shown in Figure 5D. The supramolecular hyperbranched polyglycerol (HPG) is utilized as organic phase for gluing the GO nanosheets via wetspinning technology. The achieved 1D bioinspired graphene-based fiber nanocomposites show the nacre-like architecture, as shown in Figure 5E. The hydrogen bonding networks between adjacent GO nanosheets and HPG is formed, as shown in Figure 5F, leading to the enhancement in load transfer efficiency. The tensile strength of GO-HPG fiber reaches 125 \pm 10 MPa, corresponding to about 20% improvement comparable to that of neat GO fiber with tensile strength of 102 MPa.^[100] However, the electrical conductivity of rGO-HPG (\approx 0.24 S m⁻¹) is inferior to graphene fiber (\approx 250 S cm⁻¹).^[100]

Other natural macromolecules such as silk fibroin (SL) are also ideal polymer matrix for constructing the hydrogen bonding network with GO nanosheets. Hu et al.^[101] further demonstrated integrated rGO-SL nanocomposites with electrical conductivity by a spatially localized electrochemical reduction. The ultimate tensile strength reaches 300 MPa and the toughness is as high as 2.8 MJ m⁻³, which may be caused by additional cross-linking of silk fibroin backbones in addition to the synergistic interactions. Similar to aforementioned rGO-PVA nanocomposite, the rGO-SL also shows relatively lower electrical conductivity of 13.5 S cm⁻¹ compared with pure rGO film due to the interruption of the transfer path of electrons by the insulated SL macromolecules.

2.2.2. Ionic Bonding

Trace amounts of metal ions, incorporated in the protein structures of natural biomaterials, might result in extraordinary mechanical properties, particularly stiffness and hardness. For example, copper (Cu²⁺) and zinc (Zn²⁺) ions are found in an inner protein matrix of marine polychaete worm Nereis, and play a role in mechanical hardening of the jaws of Nereis.^[102,103] Other metal ions, such as manganese, calcium, titanium, aluminum, and iron, are also found in the insect cuticles and other organisms, enhancing their mechanical properties. For



the BGBNs, the divalent metal ions of calcium (Ca²⁺) and magnesium (Mg²⁺) were first introduced into the gallery of GO nanosheets to cross-link the adjacent GO nanosheets.^[104] First, the carboxylic acid coordinates the divalent metal ions, leading to cross-linking of adjacent GO nanosheets and bridging edges of GO nanosheets together. Then, the reactive epoxy groups on the surface of GO nanosheets initiate the ring-opening of the epoxide groups under exposure to Lewis acidic divalent metal ions of Ca^{2+} , and Mg^{2+} . The coordination forms between active groups from ring opening of the epoxide groups on the GO nanosheets and divalent metal ions in the intercalation between adjacent GO nanosheets. This proposed ionic bonding reaction mechanism is verified by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectra. Two ionic bonding modes between GO nanosheets and alkaline earth metal ions are proposed: (i) bridging the edges of the GO nanosheets with carboxylate chelates to the metal ions, and (ii) intercalating between the basal planes with alkoxide or dative bonds from carbonyl and hydroxyl groups. The experimental results reveal that the ionic bonding of coordination to bridge the edges of GO nanosheets is stronger than the intercalating basal planes of GO nanosheets. Obviously, the mechanical properties of graphene-based nanocomposites with only intercalating of metal ions would decrease, due to the increase of *d*-spacing and cross-section area of tensile sample with entering of metal ions. Thus, the size of the intercalated metal ions plays a key role in enhancing the mechanical properties of resultant graphene-based nanocomposites. The experimental results show that the mechanical properties of GO-Ca²⁺ nanocomposites are lower than that of GO-Mg²⁺ nanocomposites, because the ionic radius of Ca²⁺ is 1.06 Å, is larger than that of Mg^{2+} with radius of 0.78 Å.

On the other hand, Park, et al.^[104] found that the mechanical properties of GO paper with cross-linking of ionic bonding can be improved under repeated cyclic loading with small force and slow rate. The possible reason may be that the galleries in metal ion cross-linked GO paper were chemically annealed to obtain the best structure, in other words, the edge-bound metal ions adopted more favorable chemical interactions with the oxygen-containing groups on the surface GO nanosheets under small mechanical perturbations. For example, the tensile strength and modulus were enhanced by about 10–80%, and 10–40%, respectively, for metal ion cross-linked GO paper under four cycles of loading/unloading process. However, there is no significant change for the pure GO paper under the same processing.

Besides Ca^{2+} , Mg^{2+} , other divalent ions such as Ni^{2+} , or Co^{2+} have been used to cross-link the GO nanosheets into the 3D architecture.^[105] For example, hydrothermally treated GO nanosheets can be self-assembled into 3D scaffold with adding enough Ca^{2+} , Ni^{2+} , or Co^{2+} , as shown in **Figure 6A**. The PVA was introduced to strengthen the rGO scaffold which prevented the collapse of the structure after freeze-drying, as shown in Figure 6B. The gel-like rGO cylinder with ionic bonding is illustrated in Figure 6C. The hydrogen bonding, and ionic bonding were formed between water molecules, divalent metal ions, and the oxygen-containing groups on the surface of rGO nanosheets, as shown in Figure 6D. Compared to ionic bonding, it is easy to break weak hydrogen bonding to form



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Figure 6. Ionic bonding in bioinspired graphene-based nanocomposites. (A) Digital photos of the GO before and after hydrothermal treatment. No.1 is GO, No.2 is rGO, and No.3 to 7 are rGO cross-linked with different content of Ca²⁺. Reproduced with permission.^[105] Copyright 2010, American Chemical Society. (B) Photos of gel-like rGO cylinders cross-linked with Ni²⁺ (No.8) and Co²⁺ (No.9). Reproduced with permission.^[105] Copyright 2010, American Chemical Society. (C) Photos of the Ca²⁺ cross-linked rGO nanocomposites dried by evaporation (No.10), and after freeze drying (No.11) without (No.12) and with PVA. Reproduced with permission.^[105] Copyright 2010, American Chemical Society. (D) Schematic illustration of divalent ion linkage with GO nanosheets. Reproduced with permission.^[105] Copyright 2010, American Chemical Society. (E) Typical stress–strain curves of various ionically bonded and cross-linked GO nanocomposites under stretching. Reproduced with permission.^[106] Copyright 2014, Royal Society of Chemistry. (F) Proposed molecular structure changes for Zn²⁺ cross-linked GO nanosheets under stretching. Reproduced with permission.^[106] Copyright 2014, Royal Society of Chemistry.

channels for transferring guest molecules into the rGO cylinder scaffold. The ionic bonding cross-linking strategy provides a facile and practical route of preparing the rGO scaffold.

Different from the aforementioned filtration approaches for constructing ionically cross-linked graphene-based nanocomposites, atomic layer deposition (ALD) can be also applied to impregnate a small amount of zinc on the surface of GO nanosheets.^[106] The resultant graphene-based nanocomposites (GO-Zinc) show high mechanical properties and electrical conductivity. The tensile strength, toughness and Young's modulus of GO-Zinc reach \approx 142.2 MPa, \approx 0.32 MJ m⁻³ and \approx 35.4 GPa, which are $\approx 27\%$, $\approx 39\%$ and $\approx 20\%$ improvement compared with pure GO papers with a tensile strength of ≈112 MPa, toughness of 0.23 MJ m⁻³ and Young's modulus of \approx 29.5 GPa, as shown in Figure 6E. The reason for this improvement is attributed to the ionic bonding between zinc ions with GO nanosheets. The zinc metal is infiltrated into GO paper through ALD process, in which the H₂O is utilized to be an oxygen source. Hydroxyl groups are formed by H₂O vapor absorbed on the surface of GO nanosheets, and react with zinc metal into the cross-linking bond between adjacent GO nanosheets, as shown in Figure 6F. In addition, the electrical conductivity of GO-Zinc is as high as ≈ 1 S cm⁻¹, corresponding to three orders of magnitude higher than that of pure GO papers. This is because the thin conductive ZnO layer deposited on the GO surface and the impregnated Zn atoms cross-linked with GO nanosheets. This highperformance GO-Zinc nanocomposites can also be used for

separation and purification technology, for example, this GO-Zinc nanocomposites can selectively separate diverse organic vapors with unimpededly permeating water.

In the aforementioned divalent ions cross-linking GO nanosheets process, the metal ions are usually added as an additional step after preparing the GO film. Recently, Yeh et al.^[107] found that the Al³⁺ can be released during vacuumassisted filtration assembling acidic GO dispersion into GO paper using porous anodized aluminum oxide (AAO) filter discs. The GO nanosheets are further cross-linked by Al³⁺ into stronger GO paper in the filtration process, which is designated as GO (AAO). To make a comparison, the control GO paper is filtrated with polymer membrane, such as Teflon, and denoted as GO (Teflon). As shown in Figure 7A,B, the resultant GO (AAO) paper is much smoother than GO (Teflon) due to that AAO discs having smoother surface than the Teflon membrane. But there is almost no difference in the cross-sectional surface morphology from scanning electron microscopy (SEM) image (inserted images in Figure 7A,B) and *d*-spacing from X-ray diffraction (XRD) (Figure 7C). However, the mechanical properties of GO (AAO) are much higher than that of GO (Teflon), and the tensile stress-strain curves are shown in Figure 7D. The tensile strength of GO (AAO) reaches 100.5 MPa, higher than GO (Teflon) paper with tensile strength of 86.9 MPa. Especially for the Young's modulus of GO (AAO), the improvement of 340% is achieved, compared to the GO (Teflon). In addition, the GO (AAO) paper remains intact in water (Figure 7E), while



Figure 7. Bioinspired GO paper filtrated through AAO and Teflon filters. A,B) Digital photos of GO (AAO) and GO (Teflon) paper (inserts showing the cross-sectional SEM images with scale bar of 2 µm). C,D) Comparison of XRD patterns and stress–strain curves of GO (AAO) and GO (Teflon) paper. E,F) GO (AAO) and GO (Teflon) paper is placed in water to check their stability. GO (Teflon) readily disintegrates in water (E), whereas GO (AAO) remains intact (F). Reproduced with permission.^[107] Copyright 2015, Nature Publishing Group.

the GO (Teflon) film disintegrates immediately without any mechanical agitation in water, and completely disperses after one day (Figure 7F).

In a previous report,^[104] the enhancement of Young's modulus with divalent ions (Ca²⁺, Mg²⁺) cross-linked GO paper is only 10%, which is far lower than GO (AAO) paper cross-linked with Al³⁺. The underlying reason is that the control GO papers used were probably already cross-linked with ionic bonding of Al³⁺ due to the obtained control GO papers from filtration with an AAO filter. Thus, the aforementioned cross-linked GO paper with Al³⁺ should involve two kinds of metal ions, however, two more additions of metal ions in the GO paper cannot further increase the mechanical properties.

2.2.3. π – π Interaction

Based on the intrinsic sp² structure of graphene, conjugated molecules, such as pyrene derivatives, have been used to construct high-performance BGBNs through cross-linking adjacent graphene nanosheets with π – π interaction. For example, a water soluble pyrene derivative (1-pyrenebutyrate) (PB) cross-linked reduced GO nanosheets into nanocomposites (rGO-PB),^[108] as

shown in Figure 8A. The mechanical properties and electrical conductivity of rGO-PB are dramatically enhanced, resulting in the tensile strength of 8.4 MPa, toughness of 0.01 MJ m⁻³, Young's modulus of 4.2 GPa, and electrical conductivity of 2 S cm⁻¹, which is seven orders of magnitude higher than the pure GO paper (6 \times 10⁻⁷ S cm⁻¹). Moreover, Liu et al.^[109] has also demonstrated that the insertion of 1-pyrenebutyric acid *N*-hydroxysuccinimide ester into graphene interlayer by $\pi - \pi$ stacking interaction could result in six orders of magnitude increase in plane-to-plane conductivity of LBL-stacked chemical vapor deposition (CVD) graphene films. However, the other small pyrene derivatives with pendant groups are capable of undergoing intermolecular bonding, such as 1-pyrene butyric acid, 1-pyrene butanol, 1-pyrene acetic acid, 1-pyrene carboxylic acid, and pyrene-1-boronic acid, are prone to aggregation in the process of constructing the graphene-based nanocomposites through π - π interaction, resulting in deleterious effects on the electrical conductivity of graphene-based nanocomposites.[109]

In addition to pyrene derivatives, both purine and pyrimidine bases from the DNA have also been utilized to cross-link graphene nanosheets through π - π interaction.^[110] Figure 8B illustrates how to achieve BGBNs through π - π cross-linking with DNA molecules or mixtures of DNA and the positively charged

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1.0 0.5 0.0 0.0

0.2

0.4

x (µm)

0.6

0.8

Figure 8. π - π interactions in bioinspired graphene-based nanocomposites. (A) Digital photograph image and cross-section morphology of rGO-PB nanocomposites with π - π interaction. Reproduced with permission.^[108] Copyright 2008, American Chemical Society. (B) Schematic illustration of synthesis of DNA-stabilized graphene aqueous suspensions and fabrication of bioinspired graphene-based nanocomposites. First, the graphite flake is oxidized, and the brown GO nanosheets are obtained. Then, GO sols are chemically reduced with hydrazine in the presence of freshly single-stranded DNA (ssDNA), resulting in stable aqueous suspension of ssDNA with functionalized graphene nanosheets (ssDNA-G). Finally, the ssDNA-G dispersion is assembled into bioinspired nanocomposites via evaporation. Reproduced with permission.^[110] Copyright 2009, Wiley-VCH. (C) AFM image of ssDNA-G sheets shows rough surface profile and thickness of about 2 nm. Reproduced with permission.^[110] Copyright 2009, Wiley-VCH.

redox protein, cytochrome c. First, graphite is chemically treated to obtain the graphene oxide nanosheets with nanometer thickness. Then, the GO sols are reduced with hydrazine into rGO nanosheets. The single-stranded DNA (ssDNA) molecules are absorbing on the surface rGO nanosheets through π - π interaction and the stable aqueous suspension of DNA-functionalized rGO nanosheets (DNA-rGO) is obtained. After selfassembly through evaporation or filtration, the ordered BGBNs are fabricated. Co-assembling of DNA-rGO nanosheets with positively charged cytochrome c can produce multifunctional graphene-based nanocomposites. In this process, the DNA-rGO sheets are the key step. Tapping mode atom force microscopy (AFM) indicates the thickness of GO nanosheets is 1-1.8 nm, as shown in Figure 8C. After functionalization with DNA molecules, the thickness of DNA-rGO sheets increases to 2-2.5 nm, significantly higher than a single graphene layer with 0.34 nm. Based on the AFM image of DNA-rGO nanosheets, the calculated thickness of DNA molecules on DNA-rGO nanosheets is about a monolayer of globular DNA molecules with thickness of 1 nm.

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The above researches discuss π - π interaction with graphene nanosheets through only one end of pyrene derivative molecules. In fact, the interface strength of graphene-based nanocomposites would be dramatically enhanced through two ends of π - π interaction between adjacent graphene nanosheets. Recently, the new long molecules with two functional pyrene groups at both ends, is synthesized to cross-link graphene nanosheets through π - π interaction,^[111] as shown in **Figure 9**A.

Polyethylene glycol (PEG) is grafted at both ends with pyrene groups, which is denoted as FPEG, and the length of FPEG can be tuned through adjusting the molecular weight of PEG. The adjacent graphene nanosheets in the nanocomposites are bridged by FPEG through π - π interaction, resulting in improvement in mechanical properties. The tensile strength of resultant nanocomposites (rGO-FPEG) increases to 45 MPa from 15 MPa for pure rGO film. The proposed fracture mechanism is as follows: in the process of stretching, the coiled FPEG chains are first stretched along the tensile direction, which absorbs a large amount of energy until the FPEG molecules are straighten up. Then, the π - π interaction between FPEG and graphene nanosheets will be broken under continuous loading resulting in further dissipation of energy. The investigation reveals that the long molecular FPEG is better for enhancing the mechanical properties of resultant rGO-FPEG nanocomposites. Because the long molecular FPEG can cross-link adjacent graphene nanosheets into a network, however, the short molecular FPEG usually only absorb on the same graphene nanosheet. On the other hand, although the π - π stacking interaction with graphene nanosheets does not disrupt the sp² conjugated network, it could change the doping density, increase the electron-hole puddles and form the scattering sites for the long molecular FPEG, resulting in the decrease of electrical conductivity of rGO-FPEG nanocomposites.

The combination of π - π interaction and covalent bonding can synergistically strengthen the graphene-based nanocomposites. For example, a new pyrene molecules with a functional

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Figure 9. π - π interactions in bioinspired graphene-based nanocomposites. (A) Schematic illustration of graphene nanosheets cross-linked with long molecules of FPEGs by π - π interaction. Reproduced with permission.^[111] Copyright 2015, Elsevier. (B) Graphene nanosheets are bonded with poly(glycidyl methacrylate) containing localized pyrene groups (Py-PGMA) through π - π interaction. Reproduced with permission.^[112] Copyright 2011, Elsevier.

segmented poly(glycidyl methacrylate) (Py-PGMA) are synthesized via an atom transfer radical polymerization.^[112] One end of Py-PGMA adhere strongly to the graphene nanosheets through π - π interaction, and the other end is reactive epoxide group, which can react with epoxy matrix to form a covalent cross-linking structure, as shown in Figure 9B. The resultant graphene-based nanocomposites show improvement of thermal conductivity.

2.2.4. Covalent Bonding

The linear polymer of polyallylamine (PAA) is first attempted to cross-link GO nanosheets with covalent bonding in the BGBNs (PAA-GO).^[113] The reactive amine groups on the long alky chain of PAA are hypothesized to react with epoxide and carboxylic acid groups on the GO nanosheets surface, which are suggested by chemical analysis of XPS and FTIR characterization. Although, the chemical structure of cross-linked GO nanosheets with PAA and the reaction mechanism of crosslinking have not been fully revealed yet, the mechanical properties of PAA-GO nanocomposites are indeed enhanced, for example, the tensile strength, toughness and Young's modulus are improved to 91.9 MPa, 0.21 MJ m⁻³ and 11.3 GPa from 81.9 MPa, 0.18 MJ m⁻³ and 5.8 GPa for pure GO paper, respectively. This investigation indicates that the approach of covalent bonding is extremely useful for improving the mechanical properties of BGBNs. In addition, the free and reactive amine groups on the PAA chain also are good precursors for further chemical modification to enhance the density of covalent bonding networks.

Different from the linear polymer chain of PAA, small molecules, such as glutaraldehyde (GA), can be introduced into the gallery regions to cross-link adjacent GO nanosheets into BGBNs (GO-GA).^[114] The mechanical properties of GO-GA nanocomposites are significantly enhanced, for example, the tensile strength and Young's modulus are improved to 101 MPa and 30.4 GPa from 63.6 MPa and 10.5 GPa for pure GO paper. The load-bearing capability of GO nanosheets before and after GA cross-linked is efficiently monitored by the in situ Raman spectroscopy, further confirming that the improvement of interlayer strength via covalent bonding of GA plays a key role in enhancing mechanical properties of resultant BGBNs of GO-GA. Furthermore, Kim et al.[115] fabricated strong GO/ diamine fibers through covalent cross-linking GO nanosheets with different lengths of diamine molecules, whose tensile strengths ranges from 275.1 to 384.3 MPa. It has been demonstrated that the tensile strength and Young's modulus are decreased with the length of diamine molecules, while the elongation at break is increased with the length of diamine molecules.

The above investigations on covalent bonding in the BGBNs, have not yet fully realized the key role of covalent bonding on enhancing mechanical properties possibly because of the



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Figure 10. Covalent bonding between borate orthoester and GO nanosheets results in very stiff bioinspired graphene-based nanocomposites. (A) Schematic illustration of the formation of the borate cross-linked network across two adjacent GO nanosheets (GO-Borate). (B) Comparison of the typical stress–strain curves of the unmodified and borate-modified nanocomposites demonstrate significant improvement in stiffness and decrease in strain to failure resulting from the formation of covalent bonding between adjacent GO nanosheets. (C) Corresponding plot of stiffness as a function of borate ion concentration in bioinspired GO-Borate nanocomposites before and after thermal annealing, demonstrating significant mechanical enhancement afforded by the thermal treatment after borate cross-linking. Reproduced with permission.^[117] Copyright 2011, Wiley-VCH.

low covalent cross-linking density. Borate ions (in very small quantities) are found to be able to significantly enhance the mechanical properties of plant tissue, especially their stiffness and strength.^[116] This is because borate ions can form covalent bonding with oxygen-containing functional groups in a variety of pH and counter ion environments in plants. Inspired by this, borate ions are utilized to covalently cross-link adjacent GO nanosheets into nanocomposites (GO-Borate).[117,118] The formation process of covalent bonding between adjacent GO nanosheets is illustrated in Figure 10A. In the fabrication process of vacuum-assisted filtration, the water molecules in the gallery region of GO paper form hydrogen bonding with epoxide and hydroxyl groups to bridge the adjacent GO nanosheets. When the borate anions are introduced by adding sodium borate solution into GO suspension, the borate orthoester bonds are formed as well as hydrogen bonding. Then, more covalent bonding within the intersheet gallery of GO paper are formed through thermal annealing. The mechanical properties of GO-Borate nanocomposites are greatly improved, for example, the tensile strength and stiffness are enhanced to

160 MPa and 110 GPa from 130 MPa and 30 GPa for unmodified GO papers, as shown in Figure 10B. With further thermal annealing, the amount of borate ortherester oligomers formation is promoted. Subsequently the tensile strength and Young's modulus of GO-Borate nanocomposites are further improved to 185 MPa, and 127 GPa, respectively. In addition, the mechanical properties of GO-Borate nanocomposite can be tuned with respect to borate concentration, as shown in Figure 10C. Thus, this kind of bioinspired strategy is anticipated to provide an improvement in the mechanical properties of other layered nanocomposites based on other 2D nanosheets, such as, Al_2O_3 platelets, and nanoclay, etc.

Furthermore, the toughness of BGBNs can be dramatically improved by constructing covalent bonding with linear molecules between adjacent GO nanosheets. For example, a long chain molecule of 10,12-pentacosadiyn-1-ol (PCDO) can be grafted on the surface of GO nanosheets via covalent bonding between the alcohol groups at the end of the PCDO and the carboxylic acids on the surface of GO nanosheets.^[119] In addition, a network of long chain molecules of PCDO is formed through cross-linking



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Figure 11. Covalent bonding between GO nanosheets and long molecules of PCDO results in ultratough bioinspired graphene-based nanocomposites. (A) Typical stress–strain curves of GO film and GO-PCDO nanocomposites. Comparison of the fracture morphology of GO (B), rGO (C), GO-PCDO (D) and rGO-PCDO (E). The edge curving of graphene nanosheets after breaking of chemical bonds during the fracture process of nanosheets with PCDO. (F) Proposed fracture mechanism of bioinspired graphene-based nanocomposites. Reproduced with permission.^[119] Copyright 2013, Wiley-VCH.

of PCDO molecules under UV irradiation through 1,4-addition polymerization of PCDO's diacetylenic units. After chemical reduction by HI, the residual groups on the GO nanosheets are then removed. Such an approach resulted in improvement in mechanical properties of PCDO cross-linked graphene-based nanocomposites (rGO-PCDO), as shown in Figure 11A. The tensile strength of bioinspired rGO-PCDO nanocomposites reaches up 129.6 MPa, corresponding to 36% improvement. The toughness, calculated from area under stress-strain curves, is as high as 3.9 MJ $\,\mathrm{m^{-3}},$ which is 117% enhancement compared to pure GO film. The unique fracture morphologies of bioinspired rGO-PCDO nanocomposites reveal the toughening mechanism of covalent bonding via PCDO molecules. GO and rGO films display smooth fracture morphology, as shown in Figure 11B,C, while GO nanosheets are pulled out with the curled edges in the GO-PCDO and rGO-PCDO nanocomposite, as shown in Figure 11D,E, indicating that much more energy have dissipated in the fracture of covalent bonding networks of PCDO between adjacent GO nanosheets. The corresponding fracture process and toughening mechanism are illustrated in Figure 11F. When the bioinspired rGO-PCDO nanocomposites are loaded, the coiled network of cross-linked PCDO molecules network is first stretched, absorbing much more energy and simultaneously leading to high tensile strain. With increased loading, the eneyne backbones of cross-linked PCDO network are broken and the covalent bonding between PCDO and GO nanosheets are destroyed, further dissipating more energy. The tensile strength of rGO-PCDO nanocomposites is further enhanced, and toughness reaches maximum after covalent bonding between PCDO network and GO nanosheets are broken. On the other hand, the electron-transfer pathway among the Z direction of GO nanosheets is also improved by the network of cross-linked PCDO molecules between adjacent GO nanosheets, resulting in high electrical conductivity of 232.29 S cm⁻¹.

Due to the low density of covalent bonding between PCDO molecules and GO nanosheets, the improvement in tensile strength of bioinspired rGO-PCDO nanocomposites is not as high as the toughness.^[119] Thus, high density covalent bonding between adjacent GO nanosheets should be much better for improving the tensile strength of BGBNs. This has been demonstrated via constructing 3D network of covalent bonding between adjacent GO nanosheets,^[120] as shown in Figure 12A. The GO nanosheets are first coated by PDA, and the polyetherimide (PEI) is introduced into the gallery of PDA modified GO nanosheets (PGA). Under a weak alkaline environment with a pH of 8.5, the catechol groups on PDA are oxidized into quinone, which would cross-link with the amine groups on PEI via covalent bonding. Thus, the cross-linking density in the bioinspired nanocomposites (PGA-PEI) can be tuned by introducing different content of PEI and the maximum mechanical properties can be achieved. For example, the mechanical properties of PGA-PEI nanocomposites increase with additions of PEI, and reach maximum value with tensile strength of 178.9 MPa and Young's modulus of 84.8 GPa at the PEI content of about 14.7 wt.%. With adding pressure in the process of vacuum-assisted filtration, the orientation of GO nanosheets in the PGA-PEI nanocomposites is further improved, resulting in high mechanical properties with tensile strength up to 209.9 MPa and Young's modulus up to 103.4 GPa, respectively, as shown in Figure 12B. However, the toughness is decreasing due to strong limitation of slippage by high density covalent bonding between adjacent GO nanosheets.

The aforementioned investigations were focused on tuning density of covalent bonding to adjust the gallery interactions between adjacent GO nanosheets in the BGBNs. Recently, an investigation on the tuning the intersheet spacing of GO nanocompoties via covalent bonding was reported.^[121] The dicarboxylic acids, diols or polyols with different length chain, were



www.MaterialsViews.com HN B Α 170 NH: 180 190 200 105 pH 8.5 210 for crosslinking (GPa) 100 HN roung's Modulus 95 90 85 HO H 80 Immersing for Crosslinking Vacuum-Assisted Crosslinking

Figure 12. Ultrahigh modulus and strength are realized through covalent cross-linking of GO nanosheets with mussel-inspired polymers. (A) Schematic illustration of PEI cross-linking two adjacent PGOs into bioinspired nanocomposites (PGO-PEI). SEM images of the fracture morphology before and after the cross-linking process. (B) Tensile strength and Young's modulus of bioinspired PGO-PEI nanocomposites obtained either by immersion or by the vacuum-assisted filtration approach. The digital photograph image demonstrates the ability of the bioinspired PGO-PEI nanocomposites fabricated by vacuum-assisted filtration strip (5 µm thick and 8 mm wide) to completely support the mass of about 220 g (weights, clamp, and string). Reproduced with permission.^[120] Copyright 2013, Wiley-VCH.

utilized to covalently cross-link the GO nanosheets through esterification reactions. The experimental results show that the intersheet spacing, Young's modulus and permeation fluxes of resultant graphene-based nanocomposites generally increase with increasing the length of the molecular chain of dicarboxylic acid, from oxalic acid, propandioic acid, succinic acid, hexanedioic acid, to octanedioic acid. However, due to hydrophilic substituent of hydroxyl group favoring the penetration of hydrated ions in the diols or polyols, the intersheet spacing is enlarged with increasing length of hydrophobic substituents of alkane chain, such as ethylene glycol, 1,2-propylene glycol, butylene glycol, 1,6-hexylene glycol, neopentyl glycol, glycerol and pentaerythrithol, but the Young's modulus, permeation fluxes are lower than that of nanocomposites cross-linked with dicarboxylic acids. Although the precise separation of ions and molecules were demonstrated by adjusting the different chain lengths of dicarboxylic acids, dios or polyols, the mechanical properties of resultant nanocomposites were not fully characterized, making the comparison between them and other BGBNs quite difficult.

2.3. Synergistic Toughening

Natural materials, such as bone and nacre, show extraordinary mechanical properties, due to the synergy from hierarchical micro-/nanoscale structure and interfacial interactions.^[16] Bone is composed of ordered network assembled from collagen fibrils and hydroxyapatite nanocrystals through synergistic toughening, forming tough, lightweight, adaptive, and self-healing structure. These two nanophases make up about 95% of the dry weight of bone. Nacre, also shows the high damage tolerance, due to the synergistic effect from hierarchical structure and abundant interfacial interactions. These biological materials provide an excellent inspiration of synergistic toughening for constructing high-performance graphene-based

nanocomposites. A series of BGBNs with different synergistic toughening approaches have been demonstrated recently, as shown in Figure 13. For example, synergistic interfacial interactions of hydrogen and covalent bonding resulted in high toughness of rGO-CS nanocomposites with 17.7 MJ m⁻³ (Figure 13A).^[92] The synergistic building blocks of 1D nanofibers and 2D GO nanosheets lead to ultrahigh strength of rGO-CNC nanocomposites with 655 MPa.^[53] And the high fatigue-resistant rGO-DWNT-PCDO nanocomposites were also demonstrated with synergistic effects of interfacial interactions and building blocks together (Figure 13E).^[122] In the following sections, the synergistic toughening approaches for constructing BGBNs are categorized into: i) synergy from interfacial interactions, ii) synergy from building blocks, and iii) synergy from combination of interfacial interactions and building blocks, which is discussed in detail below. Furthermore, based on the relative strength of different interfacial interactions, the corresponding synergistic toughening mechanism is proposed that the sequential breakage of strong and weak interactions during continual stressing process results in synergy effect. In addition, the electrical conductivity is also discussed and compared to provide a complementary reference for constructing integrated high-performance multifunctional BGBNs with applications in the fileds of flexible energy devices.

2.3.1. Synergy from Interfacial Interactions

In fact, there are more than one kind of force involved in BGBNs, which means interfacial interactions are interdependent on each other. Such nonadditive behavior of interfacial interactions is the essence of synergistic effect, which could be illustrated by a proposed cartoon, as shown in **Figure 14**. For example, 1 and 2 represents different interfacial interactions. Because of different intrinsic properties, 1 and 2 cannot independently roll on the smooth substrate. However, if 1 and 2

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Figure 13. Bioinspired graphene-based nanocomposites fabricated with different synergistic toughening approaches: (A) Hydrogen bonding and covalent bonding; (B) Hydrogen bonding and ionic bonding; (C) Ionic bonding and covalent bonding; (D) With 1D nanofibrils; (E) With 2D molybdenum disulfide; (F) With 2D montmorillonite; and (G) With carbon nanotubes and covalent bonding. The synergistic toughening results in dramatic enhancement of tensile strength, Young's modulus, and toughness. Furthermore, other properties such as fatigue, fire retardancy can be obtained by incorporating second building blocks including 1D nanofibrils and 2D nanoplatelets.

matched very well, the combination of 1 and 2 can easily roll on the smooth substrate. That means that if the 1 and 2 maximally play their functions together, much higher performance or new functions will be created. And this is the essence of synergistic effect. In terms of BGBNs, the high integrated performance can be realized by properly combining different interfacial interactions, which will be discussed in detail in the following sections.



Figure 14. Illustration of synergy through a proposed cartoon: The structures 1 and 2 represent different interfacial interactions. 1 and 2 cannot independently roll on the smooth substrate due to their different intrinsic properties. However, when 1 and 2 match each other very well, the combination of 1 and 2 can easily roll on the smooth substrate, meaning that 1 and 2 maximally play their functions together and much higher performance or new functions will be created. This is the essence of synergistic effect.

Hydrogen Bonding and Covalent Bonding: To achieve synergy between hydrogen and covalent bonding, biomolecules are a good choice due to their abundant functional groups, such as chitosan (CS),^[92] and dopamine (DA).^[62] For example, CS with many functional groups of hydroxyl and amine, can be cross-linked to adjacent GO nanosheets to form bioinspired nanocomposites (rGO-CS),^[92] as shown in Figure 13A. The synergistic effect from hydrogen and covalent bonding can be achieved through tuning the CS content in the fabrication process. As shown in Figure 15A, the flow force can easily spread the CS molecular chains on the surface of GO nanosheets at the low CS content, resulting in an exposure of buried reaction sites (amine) on CS molecular chain. These active sites groups on CS can further react with carboxyl groups on the surface of GO sheets. When the CS content is too high, the strong repulsion resulting from "electrosteric stabilization" during assembly process, leads to coiled CS with intramolecular hydrogen bonding. Thus, the distribution of CS molecular chains on the GO sheets cannot be obtained, and the chemical reaction between CS molecular chains and GO sheets cannot occur.

The synergistic effect from hydrogen and covalent bonding results in high mechanical properties of rGO-CS nanocomposites. For example, the tensile strength of rGO-CS reaches up to 526.7 MPa, and toughness is as high as 17.7 MJ m⁻³, corresponding to 1.6 and 3.9 times higher than that of rGO



Figure 15. Synergistic effect from hydrogen and covalent bonding. (A) Proposed mechanism of interfacial interactions between CS and GO nanosheets. (B) Comparison of tensile stress-strain curves of CS film (Curve 5), GO film (Curve 1), rGO film (Curve 2), GO-CS (Curve 3) and rGO-CS nanocomposites (Curve 4). Lateral view profiles of fracture surface morphology of rGO film (C) and rGO-CS nanocomposites (D). Reproduced with permission.^[92] Copyright 2015, American Chemical Society.

and CS film, respectively, as shown in Figure 15B. The lateral view images of fracture morphology of rGO-CS nanocomosites are shown in Figure 15C. Compared to fracture surface of rGO film, the rGO-CS nanocomposites show that the graphene nanosheets are raggedly pull-out and dramatically curled their edges in the fracture process. In the first stage of the fracture process, the graphene nanosheets begin to slip, resulting in breaking of the weak hydrogen bonding between CS molecule chains and graphene nanosheets. With additional loading, the coiled CS molecule chains are continuously stretched until the covalent bonding between CS and graphene nanosheets is broken. On the other hand, the bioinspired strategy with a high content of graphene (≈94.4 wt%) also endows the rGO-CS nanocomposites with a high electrical conductivity of 155.3 \pm 4.0 S cm⁻¹, a little lower than pure rGO film due to the insertion of insulated CS molecules into adjacent rGO nanosheets.

DA is a mimic of mussel adhesive protein, and contains both the functional catechol and amine groups, which is good choice for constructing BGBNs with synergistic interactions of hydrogen bonding and covalent bonding. Cui et al.^[62] demonstrated an integrated BGBNs (rGO-PDA) through cross-linking of GO nanosheets with DA. The DA molecules not only react with GO sheets but also self-polymerize into PDA. The covalent bonding network is formed between PDA and adjacent GO nanosheets, and at the same time, the hydrogen bonding between PDA chains and GO nanosheets is also formed. The tensile strength of rGO-PDA nanocomposites is dramatically improved by covalent bonding network to 204.9 MPa, higher than that of rGO-PCDO nanocomposites (129.6 MPa) with covalent bonding of linear molecules of PCDO.^[119] In addition, the toughness of rGO-PDA nanocomposites is as high as 4.0 MJ m^{-3} , slightly higher than rGO-PCDO nanocompoistes

with 3.92 MJ m⁻³, because of the abundant hydrogen bonding network between PDA and adjacent GO nanosheets. However, the electrical conductivity of rGO-PDA nanocomposites (18.5 S cm⁻¹) is much lower than that of rGO-PCDO nanocomposites with the π -conjugated backbones, even inferior to pure rGO film (44.8 S cm⁻¹).

Compared to the 2D film BGBNs, the 1D fiber BGBNs show much higher mechanical properties.^[99,123-134] Hu et al.^[123] demonstrated high mechanical performance 1D fiber BGBNs through constructing the synergistic hydrogen and covalent bonding. The assembly process of the 1D fiber BGBNs is illustrated in Figure 16A-C. The giant GO nanosheets with average diameter of 13 µm can form lyotropic liquid crystals (LCs) at a very low concentration. After addition of organic compound of HPG, the GO/HPG composite LCs were formed with the HPG molecules inserting themselves into the interlayer channels of GO nanosheets. Then, this composite LCs were assembled into nacre-like 1D fiber BGBNs (GO-HPG) via wet-spinning approach. The cross-section of GO-HPG fiber shows layered structure of alternative GO nanosheets and HPG molecules without phase separation due to extremely high fraction of GO nanosheets, as shown in Figure 16D,E. The surface morphology of GO-HPG fiber indicates the spreading ridges along axial direction, as shown in Figure 16F,G.

The well-defined layered hierarchical structure and hydrogen bonding networks of GO-HPG result in high tensile strength with 555 MPa, and ultrahigh toughness with 18 MJ m⁻³, much higher than the aforementioned 2D BGBNs. The covalent acetal bridges between -OH groups of HPG molecules and GO nanosheets were constructed with GA. The tensile strength and Young's modulus of GO-HPG-GA were dramatically enhanced to 652 MPa, and 20.9 GPa, respectively, superior to other 2D



Figure 16. 1D bioinspired graphene-based fiber nanocomposites (GO-HPG) obtained via synergistic effect from hydrogen and covalent bonding. (A–C) LCST protocol for fabricating 1D bioinspired graphene-based fiber nanocomposites: (A) formation of GO LCs with uniform nanochannels, (B) incorporation of guest compounds (e.g., polymers, biomacromolecules, and nanoparticles) into the host nanochannels to give host-guest complex LCs, and (C) wet-spinning assembly of complex LCs into 1D bioinspired graphene-based fiber nanocomposites. D,E), and (F,G) SEM images of cross-section morphology and surface morphology of dried GO-HPG fiber nanocomposites with different magnification. Scale bars, 3 µm (D,G), 500 nm (E) and 5 µm (F). H) Comparison of 1D bioinspired GO-HPG fiber nanocomposite with nacre, bone, and reported other layer-structured nanocomposites in terms of strength and toughness. Reproduced with permission.^[123] Copyright 2013, Nature Publishing Group.

film BGBNs, as shown in Figure 16H. After reduced by hydroiodic acid-acetic acid (HI-AcOH), the electrical conductivity of rGO-HPG is only 52.61 S cm⁻¹, which is much lower than that of graphene fiber (\approx 250 S cm⁻¹)^[100] due to the high content of insulated HPG molecules (23.2 wt%).

Hydrogen Bonding and Ionic Bonding: Xu et al.^[126] assembled giant GO nanosheets with high aspect ratios (**Figure 17**A) into 1D fiber BGBNs with highly ordered alignment of GO nanosheets. To further improve the mechanical properties of resulted 1D fiber BGBNs, the divalent ionic cross-linking was introduced with different divalent ions, containing Ca²⁺ and Cu²⁺. The synergistic interactions of hydrogen and ionic bonding were formed, resulting in significant improvement of mechanical properties, as shown in Figure 17B. For example, the 1D fiber BGBNs of GO-Cu²⁺, and GO-Ca²⁺, achieve the tensile strength of 274.3 MPa, and 364.4 MPa, from 184.6 MPa for control sample, respectively. After chemical reduction of HI, the tensile strength of rGO-Cu²⁺, and rGO-Ca²⁺ fiber nanocomposites reach as high as 408.6 MPa, and 501.5 MPa.

The fracture morphology of 1D fiber BGBNs displays the characteristic pull-out of GO nanosheets, as shown in Figure 17C. In the divalent cross-linked 1D fiber BGBNs, the ionic bonding is formed through bridging oxygen-containing groups on the GO surface and boundaries with divalent ions, resulting in the synergistic interactions with hydrogen bonding between residual oxygen functional groups of rGO nanosheets. Thus, the constituent of graphene nanosheets endure a pulling force to slide from the stacked graphene blocks along tensile stretching in the fiber axial direction. Compared with 2D film BGBNs, wrinkles on the layered graphene nanosheets in 1D fiber BGBNs can contribute to much higher mechanical performance. When loading is increased, the hydrogen bonds break first, followed by breaking of the ionic bonds as illustrated in the tension-shear model shown in Figure 17D.

In addition to excellent mechanical properties, the giant GO nanosheets (average lateral size of ~18.5 µm) also render the pure rGO fiber with high electrical conductivity of 390 S cm⁻¹, which is much higher than that of previous graphene fiber (~250 S cm⁻¹)^[100] composed of small size of GO nanosheets (average lateral size of ~0.81 µm). Moreover, after introducing divalent ionic bonding, the electrical conductivity of rGO-Cu²⁺ (380 S cm⁻¹) and rGO-Ca²⁺ (410 S cm⁻¹) fiber nanocomposites is comparable and even superior to pure rGO fiber, indicating little effect of ionic bonding on the electrical conductivity of resultant BGBNs.

Ionic Bonding and Covalent Bonding: Zhang et al.^[135] demonstrated the synergistic interactions of ionic and covalent bonding in the 1D fiber BGBNs. The ionic bonding between adjacent GO nanosheets is constructed through the introduction of diavalent ion of Ca^{2+} in the spinning process of graphene-based fiber and then the covalent bonding is formed with GO sheets by 10,12-pentacosadiyn-1-ol (PCDO), as shown in **Figure 18**A. The content of Ca^{2+} is difficult to be optimized due to its introduction in the spinning process. However, the amount of PCDO molecules grafted onto GO nanosheets can be tuned through annealing GO nanosheets at different temperatures. With the annealing temperature increasing, the specific oxygen-containing functional groups are gradually removed. The PCDO content in the final 1D fiber BGBNs also decreases. Thus the synergistic effects from ionic and covalent



Figure 17. 1D bioinspired graphene-based fiber nanocomposites via synergistic effect from hydrogen and ionic bonding. (A) SEM image of GGO nanosheets with lateral size of about 18.5 µm. (B) Representative tensile stress–strain curves of the GGO fibers and RGG fibers. (C) SEM images of fracture surfaces of RGG-Ca²⁺ fibers. (D) Proposed deformation mechanism model of bioinspired graphene-based fiber nanocomposites under tensile stress. The dashed lines indicate the hydrogen bonding and coordinative ionic bonding bridging adjacent GO sheets. Reproduced with permission.^[126] Copyright 2013, Wiley-VCH.

bonding are achieved, leading to the better mechanical properties of 1D fiber BGBNs. The corresponding tensile stressstrain curves are shown in Figure 18B. The rGO-Ca²⁺-PCDO-II fiber nanocomposite reaches the maximum tensile strength of 842.6 MPa and toughness of 15.8 MJ m^{-3} at the PCDO content of 3.61 wt.%. The changes in the mechanical properties of the rGO-Ca²⁺-PCDO fiber nanocomposites having different content of PCDO molecules are shown in Figure 18C, D. Besides the synergistic interactions of ionic and covalent bonding, the large size of GO nanosheets may be another reason for higher mechanical properties. Recently, Hu et al.^[134] fabricated strong 1D fiber BGBNs. The average diameter of GO nanosheets is about 20 µm. The 1D fiber BGBNs were assembled with sodium alginate (SA) via wet-spinning technique. The resultant GO-SA fiber nanocomposite shows the tensile strength of 784.9 MPa. In the GO-Ca²⁺-PCDO fiber nanocomposites,^[135] the average size of GO nanosheets reaches about 30.5 µm, which may be better for improving the mechanical properties of 1D fiber BGBNs.

The proposed fracture mechanism of $rGO-Ca^{2+}-PCDO$ fiber nanocomposites for illustrating the synergistic toughening of ionic and covalent bonding is shown in the Figure 18E. In the fracture process of the rGO-Ca²⁺-PCDO fiber nanocomposites, the coiled PCDO molecules are first stretched along the direction of loading, triggering slippage of adjacent rGO nanosheets, and resulting in energy dissipation. With increased loading, the bridge of Ca²⁺ ionic bonding starts to break. Finally, the covalent bonding between PCDO molecules and adjacent rGO sheets begins to fracture. The tensile strength of rGO-Ca²⁺-PCDO fiber nanocomposites is further improved. As shown in Figure 18G, the rGO nanosheets in the rGO-Ca²⁺-PCDO fiber nanocomposites are pulled out with curled-edge morphology different from the fracture morphology of rGO-Ca²⁺ fiber (Figure 18F).

It is thus clear that synergistic interfacial interactions not only enhance the ultimate strength but also improve the toughness of BGBNs. Meanwhile, the electrical conductivity of the rGO-Ca²⁺-PCDO fiber nanocomposites also reach up to 292.4 S cm⁻¹ due to the π -conjugated backbones of polymerized PCDO similar to previous rGO-PCDO film nanocomposites, which could be useful for fabricating flexible electrodes, wearable supercapacitors, and intelligent devices. Yet, the great challenge remains to optimize this synergistic effect by carefully controlling the ratios of different interactions. Much more work need to be done for precisely tuning the synergistic effect to obtain the integrated high tensile strength and toughness of BGBNs.

2.3.2. Synergy from Building Blocks

As discovered in the natural nacre, the 1D nanofibrillar chitin and 2D aragonite calcium carbonate platelets also play a key role in extraordinary mechanical properties of nacre. This typical combination of 1D and 2D building blocks in nacre provides an inspiration for constructing the ternary nanocomposites. Zhang, et al.^[136] demonstrated the synergistic effect from 1D CNTs and 2D nanoclay in the ternary nanocomposites of nylon-6(PA6)/CNT-nanoclay. The unique ternary nanostructure was achieved, resulting in notable improvement in

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Figure 18. Ultrastrong 1D bioinspired graphene-based fiber nanocomposites via synergistic effect from ionic and covalent bonding. (A) Schematic illustration of the preparation process for the bioinspired rGO-Ca²⁺-PCDO fiber nanocomposites. (B) Typical stress–strain curves of GO-Ca²⁺-II fiber (Curve 1), rGO-Ca²⁺-II fiber (Curve 2), GO-Ca²⁺-PCDO-II fiber (Curve 3), and rGO-Ca²⁺-PCDO-II fiber (Curve 4). (C,D) The strength and toughness of bioinspired rGO-Ca²⁺-PCDO fiber nanocomposites with different PCDO content. (E) The proposed fracture mode of bioinspired rGO-Ca²⁺-PCDO fiber nanocomposites under stretching. (F) The fracture morphology of rGO-Ca²⁺-II fiber shows smooth surface of rGO nanosheets. (G) rGO-Ca²⁺-PCDO-II fiber nanocomposites shows the pullout of rGO nanosheets with curled-edge morphology. Reproduced with permission.^[135] Copyright 2016, Wiley-VCH.

mechanical properties by incorporation of only 1 wt.% CNTnanoclay hybrid filler in the matrix of PA6. Prasad et al.^[137] further investigated the synergistic effect from 1D CNTs and 2D graphene in the ternary nanocomposites based on the matrix of PVA. These aforementioned studies further confirmed that the unique synergistic effect from building blocks plays a key role in enhancing the mechanical properties of nanocomposites. Recent studies revealed that the synergistic effect from building blocks are very effective for improving the mechanical properties of BGBNs. The ternary BGBNs can be achieved through incorporating 1D nanofibers, including CNTs, nanofibrillar, and 2D platelets, such as molybdenum disulfide (MoS₂), nanoclay, and many others. Not only the integrated mechanical properties can be obtained through synergistic effect from building blocks with graphene sheets, but also new functional properties are achieved. Several typical samples on the synergistic effect from 1D and 2D building blocks with graphene sheets are discussed in detail in the following section.

Synergistic Effect with 1D Nanofibrils: Shin et al.^[138] fabricated supertough fiber nanocomposite through constructing the ternary hierarchical structure based on single-walled carbon nanotubes (SWNTs) and reduced graphene oxide flakes (RGOF).The strong interactions between SWNTs and RGOFs can establish an interconnected network under correct proportions of SWNTs



Figure 19. Ultrarobust bioinspired graphene-based nanocomposites via synergistic effect from 1D CNCs and 2D GO nanosheets. (A) Schematic illustration of the fabrication of bioinspired GO-CNCs nanocomposites via LBL technique. (B,C) Comparison of the mechanical properties between GO-CNCs nanocomposites with other bioinspired graphene-based nanocomposites in different coordinates. Reproduced with permission.^[53] Copyright 2016, Wiley-VCH.

and RGOFs with ratio of 1:1. The oxygen-containing groups and aromatic regions with unoxidized benzene rings in RGOFs can form strong π - π interactions with SWNTs. The hydrogen bonding occurs between sodium dodecyl benzene sulfonate that is associated with SWNTs and carboxyl groups on RGOFs. Thus, synergistic effect from SWNTs and RGOFs, and interfacial interactions of hydrogen bonding and π - π interactions lead to excellent mechanical properties with the tensile strength of 570 MPa and super gravimetric toughness of 1000 J g⁻¹, far exceeding spider dragline silk (165 J g⁻¹) and Kevlar fiber (78 J g⁻¹). Jalili et al.^[139] found that the polarity of the solvents is conducive to self-assembly of liquid crystal GO dispersions, and also instrumental in the formation of extensive hydrogen bonding. The steric hindrance between the highly charged GO nanosheets can overcome the unfavorable loss of rotational entropy associated with ordering. Thus, the self-oriented bioinspired GO/SWNTs nanocomposites with superior mechanical properties can be tailor-made in the process of self-assembly.

Recently, Xiong et al.^[53] fabricated ultra stiff ternary bioinspired nanocomposites through assembling the 2D GO nanosheets with high aspect ratio of 1D cellulose nanocrystals (CNCs) via LBL technique, as shown in **Figure 19**A. Due to anionic properties of CNCs component and GO nanosheets, the CNCs were modified with a cationic PEI to incorporate positively charged surface functionalities in LBL processing. The positively charged PEI sheath on CNCs component facilitates strong ionic interactions with GO nanosheets. The GO nanosheets then form conformal shells on the crossjunctions of the dense CNCs network through synergistic ionic interactions and hydrogen bonding. Thus, the local torques of the GO-jointed CNCs mediate the global deformation of ternary nanocomposites. The excessive mechanical energy is dissipating by reorientation and displacement of the confined CNCs during deformation, leading to high tensile strength of 655 MPa and record elastic modulus of 169 GPa. Figure 19B,C show comparison of toughness versus modulus and ultimate stress versus modulus between the GO-CNC ternary nanocomposite with other BGBNs. The "boomerang" like envelop reflects the traded-off between strength and toughness of materials, which is caused by conflicting mechanisms for increasing strength on one hand, and compliance on the other hand. The tensile strength and elastic modulus of ternary rGO-CNCs nanocomposites reach a record value, far superior than other BGBNs. This design principle of ternary nanocomposites combines two different classical components of 1D CNCs, and 2D GO nanosheets into bioinspired nanocomposites with very low polymer content, thus eliminating the overwhelming presence of the soft and weak polymer matrix. The synergistic interactions emanating from 1D rigid CNCs and 2D flexible GO nanosheets result in high strength and excellent modulus. However, the electrical conductivity of the ternary rGO-CNCs nanocomposites is only 50 S cm⁻¹, which is far inferior to pure rGO film (120 S cm⁻¹).





Figure 20. Synergistic effect from building blocks of ID DWNTs and 2D GO nanosheets, and covalent bonding with PCDO molecules. (A) Typical strain-stress curves of GO film (curve 1), rGO film (curve 2), GO-DWNT-V hybrid materials (curve 3), GO-DWNT-PCDO-V nanocomposites (curve 4), and rGO-DWNT-PCDO-V nanocomposites (curve 5). (B) The front and side view fracture morphology ofrGO-DWNT-PCDO-V nanocomposites after tensile testing. (C) The proposed fracture mechanism of rGO-DWNT-PCDO-V nanocomposites. (D) Tensile fatigue testing of GO film, GO-DWNT hybrid layered materials, and rGO-DWNT-PCDO-V nanocomposites. (E) The fracture morphology rGO-DWNT-PCDO-V nanocomposite after fatigue testing. Reproduced with permission.^[122] Copyright 2015, American Chemical Society.

On the other hand, the integrated high-performance ternary BGBNs are achieved through constructing the synergistic effects from 1D double-walled carbon nanotubes (DWNTs) and covalent bonding of PCDO molecules.^[122] The typical tensile stress-strain curves of ternary rGO-DWNT-PCDO nanocomposites are shown in Figure 20A. The tensile strength and toughness reach 374.1 MPa, and 9.2 MJ m⁻³, respectively. Figure 20B shows the front and side view fracture morphology of ternary rGO-DWNTs-PCDO nanocomposites. The DWNTs are pulled out along the direction of tensile stretching, and the pulled-out rGO nanosheets are curled due to the breaking of covalent bonds within PCDO molecules. The hydrogen bonding, π - π interactions, and covalent bonding are gradually broken in the stretching process. The proposed fracture mechanism is shown in Figure 20C. First, the slippage between adjacent rGO nanosheets happens under stretching, and the randomly dispersed DWNTs bridge rGO nanosheets, and resist the sliding, resulting in stress uniformly dispersed along the surface of rGO nanosheets. When increased loading, the randomly DWNTs and coiled PCDO molecule chains are gradually stretched, leading to additional energy dissipation. Before breaking of the π - π interaction between DWNTs and

0

10¹ 10² 10³ 10⁴ 10⁵ 10⁶

Number of Cycles to Failure (N)

10[°] In

> rGO nanosheets, the DWNTs are pulled out, resulting in large plastic deformation. Finally, the covalent bonds are broken, and the external force induces the curling of edge of the rGO sheets covalently grafted with PCDO molecules.

> In this ternary rGO-DWNT-PCDO nanocomposites, the synergistic effect occurs from the building blocks of 1D DWNTs and 2D rGO nanosheets, and also from π - π interaction and covalent bonding. This kind of compounded synergistic effect not only results in integrated high tensile strength and toughness, but also in extraordinary fatigue properties, as shown in Figure 20D. The fatigue life of ternary rGO-DWNT-PCDO nanocomposites is almost five orders of magnitude higher than that of binary GO-DWNT nanocomposites under same stress level. The crack propagation was deflected by 1D DWNTs via crack bridging and pull-out, and concurrently, the crack propagation was also suppressed by 2D rGO nanosheets. As shown in Figure 20E, the 1D DWNTs are heavily curled as compared with DWNTs during static tensile testing, further revealing the crack-bridging abilities of 1D DWNTs for suppressing crack propagation. Different from the rGO-CNCs nanocomposites with relatively low electrical conductivity, the ternary rGO-DWNTs-PCDO nanocomposites possess high electrical



Figure 21. Synergistic effect with 2D MoS₂ platelets. (A) Schematic illustration of the preparation process of ternary bioinspired GO-MoS₂-TPU nanocomposites. (B) Typical stress–strain curves of GO films (curve 1), GO-TPU (curve 2), rGO-TPU (curve 3) binary and GO-MoS₂-TPU (curve 4), ternary rGO-MoS₂-TPU (curve 5) nanocomposites. (C) Proposed synergistic fracture mechanism and (D) corresponding fracture morphology of rGO-MoS₂-TPU ternary nanocomposites. Reproduced with permission.^[142] Copyright 2015, American Chemical Society.

conductivity of 394.0 \pm 6.8 S cm⁻¹, which should be attributed to the synergistic transfer path of electron from1D DWNTs and π -conjugated backbones of cross-linked PCDO molecules.

Synergistic Effect with 2D Platelets: 2D platelets usually demonstrate unique intrinsic properties. For example, molybdenum disulfide (MoS₂) nanosheets exhibit excellent lubricant and mechanical properties,^[140,141] and montmorillonite (MMT) nanosheets work well as fire-retardant components used in the nanocomposites.^[29,31,32] Recently, the ternary BGBNs have been reported through synergistic effect frombuilding blocks of GO nanosheets with MoS2,^[142] and MMT platelets.^[143,144] Wan et al.^[142] assembled GO nanosheets, MoS₂ nanosheets, thermoplastic polyurethane (TPU) into the ternary nanocomposites of rGO-MoS2-TPU via vacuum-assisted filtration, as shown in Figure 21A. To achieve the maximum lubrication of MoS₂ in the rGO-MoS₂-TPU nanocomposites, it was found that the optimum content of MoS₂ was about 4 wt.%, and the corresponding typical tensile stress-strain curves are shown in Figure 21B. If the content of MoS₂ nanosheets is higher than 4 wt.%, the MoS₂ nanosheets form excessive restacking, resulting in the defects of the ternary nanocomposites. On the other hand, crack propagation of ternary rGO-MoS2-TPU nanocomposites cannot be effectively deflected at low content of MoS₂ nanosheets, resulting in low efficiency of stress transfer.

The proposed crack propagation model is shown in Figure 21C. The hydrogen bonding between rGO nanosheets and TPU was first broken under loading. With increased loading, the friction between rGO and MoS_2 nanosheets triggers the slippage of rGO nanosheets and subsequent cracking, which is deflected by MoS_2 nanosheets. The lubrication effect comes from the interface of molybdenum and sulfur

nanolayers of MoS_2 nanosheets, leading to large strain. The cycling of crack initiation-propagation-deflection dissipate more energy until the ternary rGO-MoS₂-TPU nanocomposites are broken. The damaged MoS_2 nanosheets are absorbed on the surface of pulled-out rGO sheets, as shown in Figure 21D, further verifying the proposed fracture model. This kind of synergistic effect from 2D MoS_2 nanosheets and flexible 2D GO nanosheets results in an integrated tensile strength of 235 MPa, and toughness of 6.9 MJ m⁻³.

In addition to excellent mechanical properties, further functions can be also introduced through synergistic effect from building blocks in ternary BGBNs. Ming et al.^[144] demonstrated fire-retardant ternary BGBNs by constructing the synergistic effect from building blocks 2D GO nanosheets with 2D MMT platelets in a polymer matrix of PVA. The image of the ternary rGO-MMT-PVA nanocomposites is shown in Figure 22A. The cross-section shows the typical layered structure (Figure 22B), and the EDS of Si element originated from MMT (Figure 22C) reveals that the MMT platelets are homogenously distributed in the ternary rGO-MMT-PVA nanocomposites. TEM image of the cross-section of ternary rGO-MMT-PVA nanocomposites clearly confirm well-ordered layered structure (Figure 22D), and the amplified layered structure analysis is also demonstrated in Figure 22E. Complete element distribution of MMT is presented in Figure 22F, indicating uniform dispersion of MMT in ternary rGO-MMT-PVA nanocomposites. The optimized ratio of GO:MMT is 90:10, and then 10 wt.% PVA is introduced to achieve an integrated ternary rGO-MMT-PVA nanocomposite.

There are strong interfacial interactions between PVA, GO nanosheets and MMT platelets, including hydrogen bonding between GO nanosheets and PVA chain, and covalent bonding of







Figure 22. Synergistic effect with 2D MMT platelets. (A) Digital photograph image of rGO–MMT–PVA ternary nanocomposites. (B) SEM image of the cross-section of rGO–MMT–PVA. (C) Corresponding EDS of the Si element originating from MMT in rGO–MMT–PVA. (D) High-resolution TEM image of the cross-section of rGO–MMT–PVA shows well-ordered layered structure, which is further amplified in the blue scale section analysis in (E). (F) The complete element distribution of MMT is depicted in the EDS spectrum. (G) Tensile stress–strain curves of the GO film (Curve 1), GO–MMT–VV binary layered materials (Curve 2), rGO–MMT-VI layered materials (Curve 3), GO–MMT–PVA-IV nanocomposites (Curve 4), and rGO–MMT–PVA-IV ternary bioinspired nanocomposites (Curve 5). (H,I) The tensile strength and toughness of ternary bioinspired nanocomposites with different PVA content. (J) It took only 5 seconds to burn the silkcocoon. (K) The silk cocoon did not burn when exposed for 5 minutes with rGO–MMT–PVA ternary nanocomposites. Reproduced with permission.^[144] Copyright 2015, Royal Society of Chemistry.

Al-O-C between MMT and PVA, resulting in synergistic effect and integrated mechanical properties of ternary rGO-MMT-PVA nanocomposites with tensile strength of 356.0 MPa and toughness of 7.5 MJ m⁻³, as shown in Figure 22G–I. Furthermore, the good fire retardant properties of MMT platelets are introduced into the ternary rGO-MMT-PVA nanocomposites, as shown in Figure 22J,K. The silk cocoon placed behind ternary rGO-MMT-PVA nanocomposites did not catch fire even upon prolonged exposure to flame for 5 minutes, while the same silk cocoon was immediately burned without protection of ternary rGO-MMT-PVA nanocomposites. Although some multifunctional performances are introduced for these ternary nanocomposites, the electrical conductivity of rGO-MMT-PVA and rGO-MOS₂-TPU nanocomposites is still lower than that of pure rGO film due to adding insulated components.

3. Applications

There are many reviews describing the application of graphenebased nanocomposites in energy devices.^[1,3,5–7,9–15,145] Graphene-based nanocomposites inspired from nacre including 1D fiber and 2D film show unique hierarchical structure and physical performance including mechanical and electrical properties, which are suitable for constructing many flexible energy devices, for example, organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs), actuators, nanogenerators, and supercapacitors, etc. These devices are lightweight, and have good flexibility and high performance. However, it should be emphasized that the bioinspired strategies for integrated mechanical properties may be at the cost of



other essential performance of specific flexible energy devices. Thus, it is of great significance to balance these performances when fabricating high-performance flexible energy devices. The recent process and challenges related to these energy conversion devices will be discussed in detail below.

3.1. Organic Photovoltaic Devices (OPVs)

The OPVs devices, consisting of transparent electrodes and active layers, can produce electricity by converting solar energy. Under illumination of light, excimers are generated from active layers, and then the charge separation occurs at the conjugated polymer-based p-n junctions. The transparent conductive electrodes of OPVs devices are usually build from the graphene materials, such as rGO film.^[146] For example, the 16 nm thick rGO film demonstrates a transmittance of 65%, and the resultant OPVs devices also show good flexibility, sustaining thousands of cycles of bending at a tensile strain of 2.9%.^[147] Kymakis et al.^[148] applied laser reduction technique to reduce the GO film. Although the transmittance of 20 nm thick rGO film is only 44%, the resultant OPVs devices exhibit high power efficiency of 1.1%, which is an order of magnitude higher than that of OPVs devices based on chemically reduced GO film.

Compared to the OPVs devices with ITO electrodes, the OPVs devices based on rGO show lower power efficiency, due to the low conductivity of rGO electrodes. Chemical vapor deposition (CVD) is an optimal approach for obtaining high quality graphene film with high optical transparencies and low sheet resistances. De Arco, et al.^[149] reported the flexible highperformance CVD-graphene based OPVs devices with power efficiency of 1.18%, which can work very well at bending angles up to 138°. After introducing the metal grids,^[150,151] such as Au, Ag, Ti, the sheet resistance of CVD-graphene can be further reduced, resulting in high power efficiency. The other alternative way to improve the conductance of graphene films is by incorporation of the conducting polymer, such poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) as (PEDOT:PSS),^[152,153] where the resultant OPVs devices show high power efficiency. Yu et al.^[154] designed an OPVs assembled by GO nanosheets chemically grafted with CH2OHterminated poly(3-hexylthiophene) (P3HT). The P3HT-grafted GO nanosheets (G-P3HT) facilitated the structure/property characterization and device fabrication due to G-P3HT's organic soluble property. The covalent linkage and the strong electronic interactions between the P3HT and GO nanosheets resulted in high power conversion efficiency, as high as 200% compared to the P3HT/C60 counterpart under AM 1.5 illumination (100 mW cm⁻²). The resultant power conversion efficiency is about 0.61%, indicating the G-P3HT/C₆₀ bilayer photovoltaic devices are also more efficient.

3.2. Organic Field-Effect Transistors

The BGBNs could also be used as highly efficient active electronic materials or as electrodes in various nanodevices, rendering themas promising candidates for replacing traditional silicon, ITO, metal, gold, or organic film-based materials in the field of nanoelectronics. Ou, et al.^[155] reported high quality BGBNs, which is demonstrated in organic fieldeffect transistors (OFETs) as efficient source/drain electrodes. **Figure 23**A schematically illustrates the fabrication process of this BGBNs. GO nanosheets and (3-aminopropyl) trimethoxysilane (APTMS), are assembled via LBL technique into uniform (APTMS/GO)N nanocomposites, in which APTMS works as a covalent cross-linking agent. After thermal reduction, the resultant (APTMS/RGO)N nanocomposites retain their orderly layered structure very well, and they can be employed as highly stable source/drain electrodes in OFETs.

The transfer characteristics of the OFETs based on bioinspired (APTMS/RGO)N nanocomposites having different number of bilayers, and Au films with a thickness of 40 nm as source/drain electrodes were compared, as shown in Figure 23B. The clear field-effect behavior is achieved for Au and bioinspired (APTMS/RGO)N nanocomposites OFETs, in which the drain-source current (I_{DS}) increases with increasing gate voltage $(V_{\rm G})$. The results show that the performance of OFETs based on bioinspired (APTMS/RGO)N nanocomposites is gradually improved with increasing of the number of bilayers of (APTMS/RGO)N. Moreover, when the number of bilayers exceeds 2 (only about 2.7 nm), the corresponding OFETs show better performance than that of the OFETs based on Au electrode. Figure 23C shows the contact resistances of OFETs based on bioinspired (APTMS/RGO)N nanocomposites with different bilayers. The data indicates that the contact resistance decreases to 0.09 M Ω cm for bilayers of 3, 4, and 5, which is only twentieth of OFETs based on Au electrode. These results further verify that the low contact resistance of OFETs based on bioinspired (APTMS/RGO)N nanocomposites plays an important role in their high performance. The derived schematic energy level diagrams for CuPc/Au and CuPc/(APTMS/RGO)5 is shown in Figure 23D. The hole injection barrier (E_{HIB}) at the interface of the CuPc/Au is estimated to be 0.48 eV, which is distinctly larger than that at the interface of CuPc/(APTMS/ RGO)5 (0.27 eV). This is in accordance with the fact that the contact resistance of the OFETs based on Au electrodes is much larger than that of OFETs based on (APTMS/RGO)5 electrodes. It also further confirms that the high performance of OFETs based on (APTMS/RGO)5 electrodes could be attributed to their relatively lower contact resistance.

3.3. Actuators

BGBNs can also work as actuators converting external energy to mechanical energy, which is very useful for various flexible energy devices. The graphene-based actuators, responsive to optical,^[156] electrical,^[157] temperature,^[158] acoustic,^[159] pH,^[160] and humid^[161–164] stimuli, have been already successfully demonstrated. Zang et al.^[165] fabricated flexible actuator by controlling the folding and unfolding of crumpled graphene film onto a stretched elastomer with laminated structure. When the direct-current voltage was applied, the generated electrostatic stress deformed the graphene-elastomer nanocomposite by reducing its thickness and increasing its area more than 100%. After withdrawing the voltage, the graphene-elastomer nanocomposite recovered to its unstrained state. This kind of

www.MaterialsViews.com **B** 10⁶ =e= RGO electrode: 1 bilay by APTMS Au electrode: 40nm 10 RGO electrode: 2 bilaye RGO electrode: 3 bilaye (**Y** n) 10⁻² -¹² 10⁻³ RGO electrode: 4 bilaye **RGO electrode: 5 bilave** GO graf multi 10 10 -100-75 -50 -25 0 25 50 $V_{g}(V)$ $R_{Total} W (M\Omega cm) O$ D CuPc/Au Au CuPc/RGO RGO 9 ∆ = 0.78 eV $\Delta = 0.24 \text{ eV}$ 6 Pe Š °< 0 = 4.55 eV Au electrode: 40nm = 4.32 = 5.10 $\Phi = 4.31$ **RGO** electrode: 5 bilave RGO electrode: 4 bilayer RGO electrode: 3 bilayer LUMO Ð RGO electrode: 2 bilayer RGO electrode: 1 bilayer Ð LUMO 0 E E_{HB} = 0.48 eV 120 240 360 0 номо Channel length (µm) номо

Figure 23. Application of bioinspired graphene-based nanocomposites in organic field-effect transistors (OFETs). (A) Schematic illustration of the fabrication of (APTMS/GO)N multilayer graphene-based nanocomposites via covalent LBL method. (B) Transfer characteristics of the graphene-based nanocomposites OFETs based on the (APTMS/RGO)N (N = 1–5) electrodes at $V_{DS} = -100$ V. CuPc film is used as an active electronic material. (C) Channel width normalized R_{Total} of the OFETs based on (APTMS/RGO)N (N = 1–5) and Au (40 nm) electrodes, measured with a gate bias of -60 V. (D) Schematic energy level diagram of CuPc/Au (left) and CuPc/(APTMS/RGO)5 (right) systems. Reproduced with permission.^[155] Copyright 2013, Wiley-VCH.

unique actuation of graphene-elastomer nanocomposite indicates potential application as an artificial muscle.

Recently, Yang et al.^[166] demonstrated a reversibly photodeformable bioinspired graphene-liquid crystal elastomer (LCE) nanocomposites with superior and tunable photomechanical actuation properties upon the exposure to NIR irradiation. In this NIR-actuated system, the uniform dispersion of graphene nanosheets in the LCE matrix was achieved through π - π interactions between graphene nanosheets and LC aromatic rings, and the hydrogen bonding between the oxygen-containing groups on the graphene surface and the ester groups in LCE. This kind of actuator possesses the large strain of 35.7%, high mechanical force of 240 kPa, high initial sensitivity of lower 0.5 s, fast reversible photo-response of about 8 s, and long-term cyclability, which could be attributed to the aligned graphene, selforganization nature of liquid crystals and the entropy-driven elasticity. Furthermore, the actuator performance could be readily tailored by controlling the quality, loading content, and the alignment degree of graphene nanosheets in LCE matrix. Such bioinspired graphene-based actuator provides guidance for exploring new actuators with tunable functionalities.

The freeze casting is a novel approach developed by Tomsia et al. in 2006,^[76] and has been successfully utilized to synthesize high-performance bioinspired ceramic in 2008,^[77] and carbon nanotube aerogel.^[167] Recently, Qiu, et al.^[79] applied freeze casting technique to successfully fabricate the bioinspired graphene-based cellular monoliths through controlling the amount of oxygen-containing groups of GO nanosheets

and freezing conditions. Figure 24A-C show SEM images of bioinspired graphene-based monolith with top view (A,B) and side-view (C). The schematic illustration of the fabrication process of the ultralight and superelastic bioinspired graphenebased cellular monoliths is shown in Figure 24D. The rGO nanosheets are rejected from the forming ice under freezing, and entrapped between neighboring ice crystals, resulting in the formation of rGO-based continuous network. Due to highly anisotropic growth of the ice crystals, the rGO nanosheets are forced to align along the moving solidification front. Thus, the rGO nanosheets are concentrated and squeezed at the crystal boundaries into a highly ordered structure. Furthermore, the resulted rGO structure is strengthened by the π - π interactions between rGO nanosheets, and maintain their integrity upon thawing. This kind of bioinspired graphene-based monolith exhibits excellent resilience when released from compression. The graphene-based cellular elastomers (G-elastomers) also exhibit nearly frequency-independent piezoresistive behaviors.^[78] The dynamic deformation of graphene nanosheets under compression leads to simultaneous change in electrical resistance, which in turn, can reveal new insights about their dynamic properties. The experimental data show that the delay time as well as the maximum delay ratio was quite small, with the maximum delay ratio less than 9% at <3.5 Hz and further reduced to less than 4% at >10 Hz, as shown in Figure 24E. The stress transmission rate (v_s) of this bioinspired G-elastomers decreases with the density, as shown in Figure 24F. The G-elastomers with extremely low density show fast piezoresistive

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Figure 24. Application of bioinspired graphene-based nanocomposites for actuators. (A–D) Morphology and formation mechanism of the bioinspired graphene elastomer (G-elastomer). (A–C) Typical top-view (A,B) and side-view (C) SEM image of graphene monolith. Reproduced with permission.^[79] Copyright 2012, Nature Publishing Group. (D) Schematic of the formation mechanism of the bioinspired G-elastomer monolith by freeze casting. Reproduced with permission.^[79] Copyright 2012, Nature Publishing Group. (E) The maximum delay time and ratio in accordance with different loading frequencies of G-elastomers. Reproduced with permission.^[78] Copyright 2016, Wiley-VCH. (F) Ashby chart plotting *E/ρ* versus density for G-elastomers. The values of otherordinary elastomers and elastic foams are provided for comparison. Reproduced with permission.^[78] Copyright 2016, Wiley-VCH.

response, comparable to those of elastic foams with higher density. The main reason for this is attributed to the unique structure of the G-elastomers.

The actuators based on BGBNs have been demonstrated, and show very promising future. However, the actuation mechanism is not yet well understood and more fundamental research is needed, especially for precisely controlling hierarchical micro/-nanoscale structure and adjusting the interfacial interactions of BGBNs. It remains a great challenge to further improve the actuation performance of BGBNs for practical applications in artificial muscles, robots, and many others.

3.4. Nanogenerators

Nanogenerators (NGs) are smart devices for converting mechanical/thermal energy into electricity. Nanogenerators are typically fabricated using nano-structured piezoelectric

semiconductors,^[168] such as ZnO. Poor mechanical properties of such NGs result in their very short life time. Recently, graphene-based nanocomposites have been employed to fabricate flexible NGs. Rahman, et al.^[169] reported NGs based on GO reinforced polyvinylidene fluoride (PVDF) nanocomposites with only 0.1 wt.% GO. But the generated power efficiency was low. Lee, et al.^[170] applied CVD-graphene to replace GO nanosheets, and the resultant NGs showed improved power efficiency. The device can be stretched, rolled, twisted, and folded without scarifying the performance. The piezoelectric voltages were generated under exposure to sound waves, and the output power was 30 times higher than that of a normal graphene NGs under the same input sound pressure. Finally, Kim, et al.^[171] demonstrated highly stretchable NGs, which can harvest both mechanical and thermal energies.

The structure and interfacial interactions were not investigated in these graphene-based NGs described above. Inspired by natural electrogenetic organisms, such as the electric eels,



Figure 25. Bioinspired graphene-based nanogenerator. A) Digital photograph of flexible bioinspired GHM fabricated via vacuum filtration of CCG. B) Cross-section of the freeze dried GHM with typical layered structure. C) The setup for demonstrating hydraulic-electric energy conversion with GHM. D) Proposed illustration of the mechanism for power generation with GHM. Reproduced with permission.^[172] Copyright 2013, Wiley-VCH.

Guo et al.^[172] fabricated 2D nanofluidic NG based on bioinspired graphene-based hydrogel film nanocomposites. The flexible graphene hydrogel membrane (GHM) was assembled by chemically converted graphene (CCG) colloid via vacuum filtration, as shown in **Figure 25A**. The freeze-dried GHM shows typical layered structure, as shown in Figure 25B. There is considerable amount of oxygen-containing groups on the CCG nanosheets in GHM nanocomposites, resulting in strong interfacial interactions of hydrogen bonding between adjacent CCG nanosheets and water molecules.

The setup for testing ion transport properties through the 2D GHM is shown in Figure 25C. Nitrogen gas pressure difference was applied to produce a continuous hydraulic flow going through the GHM in vertical direction. Next, the generation of synchronous ionic current through external circuit in the opposite direction to the electrolyte flow was recorded. The proposed mechanism for the flow-induced streaming current is shown in Figure 25D. An excessive cloud of counter-ions is formed adjacent to the negatively charged channel because of CCG nanosheets surface containing oxygen-containing groups. Mobile ions in the solution migrate through the 2D nanocapillary in unipolar way, which is driven by the external hydraulic flow. Thus, the cations are separated from anions by the GHM nanocomposites, resulting in a net ionic flow. Continuous and pulse-shaped ionic current signals were received from the GHM nanocomposites depending on the input wave induced by external mechanical force. Guo et al. constructed macroscopic nanofluidic circuits based on bioinspired GHM nanocomposites with ultra-large channel width of about 10 nm. This integrated 2D nanofluidic generator based on GHM nanocomposites can convert hydraulic motion into streaming ionic current, providing the possibility of this bioinspired NGs to be utilized for harvesting electricity from footsteps and stream of body fluid, or monitoring the heartbeat. Note that although such abundant pore structure within the graphene-based NGs is not consistent with nacre-like dense structure, what they have in common is the regular and ordered structure. Thus, these kinds of bioinspired design principles of regular and ordered structure are also applicable to other 2D layered materials for functional nanofluidic devices.

The BGBNs shows better mechanical properties, more suitable for constructing flexible, stretchable and wearable NGs devices as compared with the conventional NGs made from fragile and unstable piezoelectric materials. The bioinspired strategy is a relatively simple scheme, amenable to scaling up these NGs into mass production. However, it remains a great challenge to further improve the efficiency of harvesting energy and long-term electrical stability for practical portable and flexible devices application.

3.5. Supercapacitors

Supercapacitors are promising candidates for storing energy because of their high specific power density, fast chargedischarge processes and long cycling life.^[173] The flexible supercapacitors are urgently needed for many practical application in portable/wearable devices, requiring integration of excellent electrochemical performance, and high mechanical integrity under bending, folding, and even rolling. As was discussed already, the BGBNs show integrated high mechanical and electrical properties, which can satisfy the requirements of flexible supercapacitors. Wu et al.^[174] first demonstrated the application of BGBNs in flexible

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Figure 26. Graphene-based G-PNF nanocomposite film utilized as an electrode for flexible supercapacitors. A,B) Alternatively layered G-PNF nanocomposites. C,D) Comparison of cyclic voltammograms and galvanostatic charge/discharge curves of supercapacitors of G-PNF, with control sample of PANI-NF and CCG films. Reproduced with permission.^[174] Copyright 2010, American Chemical Society.

supercapacitors. The bioinspired nanocomposites (G-PNF) were assembled from chemically converted graphene (CCG) and polyaniline nanofibers (PANI-NFs) via vacuum filtration, as shown in Figure 26A,B. The cross-section of G-PNF nanocomposites show typical layered structure, similar to the nacre-like structure in terms of regularity. The magnified SEM image (down image in Figure 25B) indicates that PANI-NFs are inserted into adjacent CCG layers, resulting in large interspaces between CCG layers with a range of 10-200 nm. The performance of supercapacitor cells based on G-PNF are shown in Figure 26C,D, by measurements using cyclic voltammetry (CV) and galvanostatic charge/discharge testing. The CVs of G-PNF shows large rectangular area, indicating the large double-layer capacitances of G-PNF-based supercapacitor. The G-PNF-based supercapacitor shows two voltage stages. The first stage is attributed to electric double layer (EDL) capacitance; the second, later stage is associated with the combination of EDL and faradaic capacitances of PANI-NF component. In addition, Wang et al.[175] also fabricated freestanding and flexible graphene/polyaniline electrode via in situ anodic electropolymerization, which demonstrates tensile strength of 12.6 MPa and a stable large electrochemical capacitance with promising application in flexible supercapacitors.

Li's group have developed technique of well dispersing CCG in water without assistance of surfactants by controlling colloidal chemistry of CCG.^[176] The resultant CCG nanosheets were self-assembled into an orientated hydrogel film via vacuum filtration.^[177–179] Recently, Yang et al.^[180] demonstrated high-performance flexible supercapacitors based on this kind

of CCG hydrogel film nanocomposites. First, the as-prepared CCG hydrogel films were utilized as a precursor to fabricate EM-CCG nanocomposites via a capillary compression procedure, as shown in Figure 27A. The CCG hydrogel film was put in volatile/non-volatile miscible solution and stirred continuously, making the water in the CCG hydrogel film to be fully exchangeable with the mixture solution. Next, the volatile liquid was removed by evaporation in the vacuum oven. Finally, the non-volatile part of the miscible solution remained. The ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate, EMIMBF₄) was selected as the non-volatile. The packing density of the EM-CCG nanocomposites can be controlled by changing the ratio of volatile and nonvolatile liquids. The cross-section of as-prepared EM-CCG nanocomposites show rather uniform lavered structure, as shown in Figure 27B,C. In fact, much more hierarchical porous structure of EM-CCG nanocomposites could be better for achieving high capacitance. The volumetric capacitance (C_{vol}) generally decreased with increasing thickness of the electrodes, and this effect was particularly prominent when the pore size was in the sub nanometer range. Figure 27D,E shows the comparison of the electrochemical capacitor (EC) performance of EM-CCG nanocomposites and the dried CCG film with different mass loading in the organic electrolyte. The results revealed that both $C_{\rm vol}$ and $E_{\rm vol-electrode}$ of the EM-CCG and CCG decreased with thickness. The EM-CCG nanocomposites displayed much slower rate of decrease than that of CCG film, indicating superior ion transport of EM-CCG nanocomposites.

The ECs based on EM-CCG nanocomposites delivered both high $C_{\rm vol}$ and $E_{\rm vol-stack}$, and the volumetric energy densities





Figure 27. Bioinspired electrolyte-mediated EM-CCG nanocomposite film. A) Digital photograph image of flexible EM-CCG nanocomposite film. B,C) Cross-section of the EM-CCG nanocomposite film containing 78.9 vol.% and 27.2vol.% of H_2SO_4 , respectively. D) Volumetric capacitance and (E) energy density as a function of the areal massloading of EM-CCG film ($\rho = 1.25$ g cm⁻³) and the dried CCG film ($\rho = 1.49$ g cm⁻³) at the current density of 0.1 A g⁻¹. Reproduced with permission.^[180] Copyright 2013, American Association for the Advancement of Science.

approaching 60 watt-hours per liter. The results revealed that this kind of bioinspired EM-CCG nanocomposites were very stable underrepeated charging/discharging or under theapplication of a constant voltage. In addition, the fabrication of EM-CCG nanocomposites is essentially compatible with the traditional cost-effective papermaking process, indicating the possibility of scaling up this EM-CCG nanocomposites and a promise for large-scale real-world applications.

Besides the aforementioned 2D film BGBNs, the 1D fiber BGBNs have been also successfully explored as supercapacitor electrode.^[128,181-189] The BGBNs for fabricating supercapacitors demonstrate several advantages: i) Their integrated mechanical properties satisfy the conventional manufacturing process of supercapacitors for flexible electronic devices such as roll-up displays, electronic papers, and intelligent cloths. ii) The high electrical conductivity. However, the BGBNs utilized as flexible electronics devices need much more hierarchical porous structure for enhancing their electronic performance, which will be conflict to improving mechanical properties via constructing dense structure like nacre. Thus, how to compromise conflict between porous structure and integrated mechanical properties will be a great challenge and target of BGBNs utilized as flexible electronics in the near future, may be 5-10 years.



Figure 28. Comparison of mechanical properties of bioinspired graphenebased nanocomposites with different interfacial interactions based on published results during the last ten years, from 2007 to 2016. The blue, pink, orange, red, and green colors represent the interfacial interactions of hydrogen bonding, ionic bonding, π - π interaction, covalent bonding, and synergistic toughening for bioinspired graphene-based nanocomposites, including 1D fiber and 2D film, respectively.



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4. Conclusions and Outlook

Since the first report on mechanically exfoliated graphene in 2004,^[43] graphene-based nanocomposites remain an exciting research topic. There are thousands papers on graphene-based nanocomposites, and many related review articles have been published. This paper is focused on reviewing the recent progress in bioinspired graphene-based nanocomposites (BGBNs), fabricated via nacre-inspired strategy. The advantages of this bioinspired strategy, compared to the traditional approaches for constructing graphene-based nanocomposites, are as follows:

 Table 2. The mechanical properties of natural nacre and BGBNs.

i) the high content of graphene nanosheets; ii) well-ordered alignment of graphene nanosheets; iii) designable interfacial interactions; and iv) high-performance physical properties. For example, four representative interfacial interactions and the corresponding synergistic toughening methods play a key role in dramatically enhancing the mechanical properties of BGBNs reported from 2007 to 2016, as shown in **Figure 28** with the corresponding data listed in **Table 2**. The blue color represents the mechanical properties of BGBNs with interfacial interaction of hydrogen bonding. The resultant mechanical properties slowly increase with different contents of hydrogen bonding because

		Nacre and BGBNs	Tensile strength (MPa)	Toughness (MJ m ⁻³)	Reference
		Nacre	200.0	2.60	[16]
		GO-PVA	80.2	0.10	[90]
		GO-PMMA	148.3	2.35	
	Hydrogen bonding	rGO-PVA	188.9	2.52	[91]
		GO-SL	300.0	2.20	[52]
		rGO-SL	300.0	2.80	[101]
Interfacial interactions		GO-CS fiber	442	9.4	[188]
		GO-HPG fiber	555	15.3	[123]
		GO-PAN fiber	452	12.3	[125]
		rGO-PVA fiber	162	1.46	[124]
		rGO-PGMA fiber	500	7.5	[127]
		GO-Ca ²⁺	125.8	0.31	[104]
		GO-Mg ²⁺	80.6	0.13	
		GO-Al ³⁺	100.5	0.23	[107]
		GO-Zn ²⁺	142.2	0.32	[106]
	Ionic bonding	rGO-Mg ²⁺ fiber	165	1.2	[99]
		rGO-Ca ²⁺ fiber	501.5	16.8	[126]
		rGO-Ag fiber	300	8.3	[189]
		GO-Ca ²⁺ fiber	412	7.2	[188]
	π - π interaction	rGO-PB	8.4	0.01	[108]
		rGO-FPEG	45.0	-	[111]
		GO-GA	101.0	0.30	[114]
		GO-Borate	185.0	0.14	[117]
	Covalent bonding	PGO-PEI	209.9	0.23	[120]
		rGO-PCDO	129.6	3.91	[119]
		GO-PAA	91.9	0.21	[113]
Synergistic toughening	$\pi extstyle \pi$ interaction and hydrogen bonding	rGO-PAPB	382.0	7.50	[70]
		rGO-PDA	204.9	4.00	[62]
	Hydrogen bonding and covalent bonding	rGO-CS	526.7	17.69	[92]
		GO-HPG-GA fiber	652	13.0	[123]
	Ionic bonding and covalent bonding	rGO-Ca ²⁺ -PCDO-II fiber	842.6	15.8	[135]
	With 1D nanofibrils	rGO-DWNT-PCDO	374.1	9.20	[122]
	With 2D platelets	rGO-MoS ₂ -TPU	235.0	6.90	[142]
		rGO-MMT-PVA	356.0	7.50	[144]

of its weak strength. Although the effect of ionic bonding on improving tensile strength has been first demonstrated by Park et al. in 2008, the enhancement in mechanical properties is very limited, as shown in pink color. More basic research is needed to optimize the radius of divalent ions and the valence state of metal ions. The π - π interaction is usually utilized to stabilize the graphene nanosheets in the organic solvent for uniform dispersion. Thus, the mechanical properties of BGBNs show relative low enhancement, as shown in orange color. Covalent bonding is very distinct and effective interfacial interaction for dramatically improving the mechanical properties of BGBNs, as shown in red color.

The extraordinary mechanical properties of natural nacre are attributed to the synergistic toughening including different building blocks and abundant interfacial interactions, such as 1D chitin, 2D CaCO₃ platelets, and hydrogen, ionic and covalent bonding. Thus, the synergistic toughening provides the unique advantage for improving the mechanical properties of BGBNs, as shown in green color in Figure 28. For example, due to the synergistic interfacial interactions of hydrogen and covalent bonding, the tensile strength and toughness of the bioinspired rGO-CS nanocomposites^[92] could reach up to 526.7 MPa and 17.69 MJ m^{-3} , respectively. The ultrastrong 1D fiber BGBNs with tensile strength of 842.6 MPa and toughness of 15.8 MJ m⁻³, are achieved through constructing synergistic interfacial interactions of ionic and covalent bonding. On the other hand, the synergistic effect can be also obtained via introducing other building blocks, such as 1D nanofibrils, and 2D platelets. The experimental results demonstrate that the ternary BGBNs not only show the improvement in mechanical properties but also in introducing additional functions. For example, the ternary rGO-DWNT-PCDO nanocomposites show excellent fatigue property.^[122] The ternary rGO-MMT-PVA nanocomposites indicate excellent fire-retardant property.^[144] The graphene's intrinsic 2D structure, allows it to be assembled into integrated multifunctional BGBNs with isotropic mechanical and electrical properties, showing very promising applications, including flexible energy devices, such as OPVs, OFET, actuators, nanogenerators, and supercapacitors.

In the future, maybe 5 to 10 years, the targets for BGBNs are proposed based on practical applications: i) The tensile strength and stiffness of BGBNs can be achieved to be comparable to carbon fiber reinforced composites, realizing application BGBNs as structural materials in aerospace and aeronautics. ii) The integrated electrical and fatigue resistant properties could be simultaneously enhanced to meet the needs of flexible and wearable electronic devices. iii) Some simple, easy operation techniques will be explored for scaling up the fabrication of BGBNs, for providing amount of BGBNs for practical applications in many fields. In a word, BGBNs are starting to make shifts from the laboratory research to real-life applications, and novel integrated multifunctional properties are anticipated to be achieved in the near future.

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- [1] X. Wang, G. Shi, Energy Environ. Sci. 2015, 8, 790.
- [2] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192.
- [3] M. Mao, J. Hu, H. Liu, Int. J. Energy Res. 2015, 39, 727.
- [4] K. Hu, D. D. Kulkarni, I. Choi, V. V. Tsukruk, Prog. Polym. Sci. 2014, 39, 1934.
- [5] G. Zhou, F. Li, H.-M. Cheng, Energy Environ. Sci. 2014, 7, 1307.
- [6] C. Xu, B. Xu, Y. Gu, Z. Xiong, J. Sun, X. S. Zhao, Energy Environ. Sci. 2013, 6, 1388.
- [7] J. Zhu, D. Yang, Z. Yin, Q. Yan, H. Zhang, Small 2014, 10, 3480.
- [8] X. Huang, X. Qi, F. Boey, H. Zhang, Chem. Soc. Rev. 2012, 41, 666.
 [9] B. Luo, S. Liu, L. Zhi, Small 2012, 8, 630.
- [10] N. O. Weiss, H. L. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, X. F. Duan, Adv. Mater. 2012, 24, 5782.
- [11] N. G. Sahoo, Y. Z. Pan, L. Li, S. H. Chan, Adv. Mater. 2012, 24, 4203.
- [12] X. J. Wan, G. K. Long, L. Huang, Y. S. Chen, Adv. Mater. 2011, 23, 5342.
- [13] S. P. Pang, Y. Hernandez, X. L. Feng, K. Mullen, Adv. Mater. 2011, 23, 2779.
- [14] G. Eda, M. Chhowalla, Adv. Mater. 2010, 22, 2392.
- [15] J.-J. Shao, W. Lv, Q.-H. Yang, Adv. Mater. 2014, 26, 5586.
- [16] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, Nat. Mater. 2015, 14, 23.
- [17] Q. Cheng, L. Jiang, Z. Tang, Acc. Chem. Res. 2014, 47, 1256.
- [18] H.-B. Yao, J. Ge, L.-B. Mao, Y.-X. Yan, S.-H. Yu, Adv. Mater. 2014, 26, 163.
- [19] H.-B. Yao, H.-Y. Fang, X.-H. Wang, S.-H. Yu, Chem. Soc. Rev. 2011, 40, 3764.
- [20] J. Wang, Q. Cheng, Z. Tang, Chem. Soc. Rev. 2012, 41, 1111.
- [21] H.-P. Cong, J.-F. Chen, S.-H. Yu, Chem. Soc. Rev. 2014, 43, 7295.
- [22] Q. Cheng, J. Duan, Q. Zhang, L. Jiang, ACS Nano 2015, 9, 2231.
- [23] M. A. Meyers, J. McKittrick, P. Y. Chen, Science 2013, 339, 773.
- [24] H. D. Espinosa, J. E. Rim, F. Barthelat, M. J. Buehler, Prog. Mater. Sci. 2009, 54, 1059.
- [25] A. R. Studart, Chem. Soc. Rev. 2016, 45, 359.
- [26] X. Q. Li, H. C. Zeng, Adv. Mater. 2012, 24, 6277.
- [27] A. Finnemore, P. Cunha, T. Shean, S. Vignolini, S. Guldin, M. Oyen, U. Steiner, *Nat. Commun.* 2012, *3*, 966.
- [28] A. R. Studart, L. J. Bonderer, L. J. Gauckler, Science 2008, 319, 1069.
- [29] H.-B. Yao, Z.-H. Tan, H.-Y. Fang, S.-H. Yu, Angew. Chem. Int. Ed. 2010, 49, 10127.
- [30] J. Wang, L. Lin, Q. Cheng, L. Jiang, Angew. Chem. Int. Ed. 2012, 51, 4676.
- [31] A. Walther, I. Bjurhager, J. M. Malho, J. Ruokolainen, L. Berglund, O. Ikkala, Angew. Chem. Int. Ed. 2010, 49, 6448.



- [32] A. Walther, I. Bjurhager, J. M. Malho, J. Pere, J. Ruokolainen, L. A. Berglund, O. Ikkala, *Nano Lett.* **2010**, *10*, 2742.
- [33] Z. Tang, N. A. Kotov, S. Magonov, B. Ozturk, Nat. Mater. 2003, 2, 413.
- [34] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamoorthy, N. A. Kotov, *Science* 2007, *318*, 80.
- [35] B. Zhu, N. Jasinski, A. Benitez, M. Noack, D. Park, A. S. Goldmann, C. Barner-Kowollik, A. Walther, Angew. Chem. Int. Ed. 2015, 54, 8653.
- [36] P. Das, J. M. Malho, K. Rahimi, F. H. Schacher, B. C. Wang, D. E. Demco, A. Walther, *Nat. Commun.* 2015, *6*, 6967.
- [37] H. Bai, F. Walsh, B. Gludovatz, B. Delattre, C. Huang, Y. Chen, A. P. Tomsia, R. O. Ritchie, *Adv. Mater.* **2016**, *28*, 50.
- [38] H. Bai, Y. Chen, B. Delattre, A. P. Tomsia, R. O. Ritchie, Sci. Adv. 2015, 1, e1500849.
- [39] H. D. Espinosa, A. L. Juster, F. J. Latourte, O. Y. Loh, D. Gregoire, P. D. Zavattieri, Nat. Commun. 2011, 2, 173.
- [40] Q. Cheng, M. Li, L. Jiang, Z. Tang, Adv. Mater. 2012, 24, 1838.
- [41] J. W. Suk, R. D. Piner, J. An, R. S. Ruoff, ACS Nano 2010, 4, 6557.
- [42] X. Wei, L. Mao, R. A. Soler-Crespo, J. T. Paci, J. Huang, S. T. Nguyen, H. D. Espinosa, *Nat. Commun.* 2015, *6*, 9029.
- [43] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
- [44] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385.
- [45] F. Liu, P. M. Ming, J. Li, Phys. Rev. B 2007, 76, 064120.
- [46] B. Peng, M. Locascio, P. Zapol, S. Li, S. L. Mielke, G. C. Schatz, H. D. Espinosa, Nat. Nanotechnol. 2008, 3, 626.
- [47] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, *Science* 2000, 287, 637.
- [48] C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayou, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer, *Science* **2006**, *312*, 1191.
- [49] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, 442, 282.
- [50] J. J. Richardson, M. Bjornmalm, F. Caruso, Science 2015, 348, 411.
- [51] S. Srivastava, N. A. Kotov, Acc. Chem. Res. 2008, 41, 1831.
- [52] K. Hu, M. K. Gupta, D. D. Kulkarni, V. V. Tsukruk, Adv. Mater. 2013, 25, 2301.
- [53] R. Xiong, K. Hu, A. M. Grant, R. Ma, W. Xu, C. Lu, X. Zhang, V. V. Tsukruk, *Adv. Mater.* **2016**, *28*, 1501.
- [54] N. A. Kotov, I. Dékány, J. H. Fendler, Adv. Mater. 1996, 8, 637.
- [55] J. H. Fendler, J. Dispersion Sci. Technol. 1999, 20, 13.
- [56] Z. Xiong, T. Gu, X. Wang, Langmuir 2014, 30, 522.
- [57] D. Yu, L. Dai, J. Phys. Chem. Lett. 2009, 1, 467.
- [58] J. Zhu, H. N. Zhang, N. A. Kotov, ACS Nano 2013, 7, 4818.
- [59] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* 2007, 448, 457.
- [60] L. Qiu, X. Yang, X. Gou, W. Yang, Z. F. Ma, G. G. Wallace, D. Li, *Chem. – Eur. J.* 2010, *16*, 10653.
- [61] C. M. Chen, Q. H. Yang, Y. G. Yang, W. Lv, Y. F. Wen, P. X. Hou, M. Z. Wang, H. M. Cheng, Adv. Mater. 2009, 21, 3007.
- [62] W. Cui, M. Li, J. Liu, B. Wang, C. Zhang, L. Jiang, Q. Cheng, ACS Nano 2014, 8, 9511.
- [63] A. Chavez-Valdez, M. S. P. Shaffer, A. R. Boccaccini, J. Phys. Chem. B 2013, 117, 1502.
- [64] Z. Xiong, C. Liao, W. Han, X. Wang, Adv. Mater. 2015, 27, 4469.
- [65] C. Li, G. Q. Shi, Adv. Mater. 2014, 26, 3992.
- [66] H. Bai, C. Li, X. Wang, G. Shi, J. Phys. Chem. C 2011, 115, 5545.
- [67] Y. Xu, K. Sheng, C. Li, G. Shi, ACS Nano 2010, 4, 4324.
- [68] H. Bai, K. Sheng, P. Zhang, C. Li, G. Shi, J. Mater. Chem. 2011, 21, 18653.
- [69] L. Huang, C. Li, W. Yuan, G. Shi, Nanoscale 2013, 5, 3780.

- [70] M. Zhang, L. Huang, J. Chen, C. Li, G. Shi, Adv. Mater. 2014, 26, 7588.
- [71] M. Zhang, W. Yuan, B. Yao, C. Li, G. Shi, ACS Appl. Mater. Interfaces 2014, 6, 3587.
- [72] Q. Liu, M. Zhang, L. Huang, Y. Li, J. Chen, C. Li, G. Shi, ACS Nano 2015, 9, 12320.
- [73] Z. Tan, M. Zhang, C. Li, S. Yu, G. Shi, ACS Appl. Mater. Interfaces 2015, 7, 15010.
- [74] Y. Xu, G. Shi, X. Duan, Acc. Chem. Res. 2015, 48, 1666.
- [75] M. Zhang, Y. Wang, L. Huang, Z. Xu, C. Li, G. Shi, Adv. Mater. 2015, 27, 6708.
- [76] S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia, *Science* 2006, 311, 515.
- [77] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Science* **2008**, *322*, 1516.
- [78] L. Qiu, M. Bulut Coskun, Y. Tang, J. Z. Liu, T. Alan, J. Ding, V.-T. Truong, D. Li, Adv. Mater. 2016, 28, 194.
- [79] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Wu, D. Li, Nat. Commun. 2012, 3, 1241.
- [80] L. Qiu, D. Liu, Y. Wang, C. Cheng, K. Zhou, J. Ding, V.-T. Truong, D. Li, Adv. Mater. 2014, 26, 3333.
- [81] C. Cheng, G. Jiang, C. J. Garvey, Y. Wang, G. P. Simon, J. Z. Liu, D. Li, Sci. Adv. 2016, 2, e1501272.
- [82] J. L. Vickery, A. J. Patil, S. Mann, Adv. Mater. 2009, 21, 2180.
- [83] S. Pei, J. Zhao, J. Du, W. Ren, H.-M. Cheng, Carbon 2010, 48, 4466.
- [84] Z. Dong, C. Jiang, H. Cheng, Y. Zhao, G. Shi, L. Jiang, L. Qu, Adv. Mater. 2012, 24, 1856.
- [85] C. Xiang, N. Behabtu, Y. Liu, H. G. Chae, C. C. Young, B. Genorio, D. E. Tsentalovich, C. Zhang, D. V. Kosynkin, J. R. Lomeda, ACS Nano 2013, 7, 1628.
- [86] R. Cruz-Silva, A. Morelos-Gomez, H.-i. Kim, H.-k. Jang, F. Tristan, S. Vega-Diaz, L. P. Rajukumar, A. L. Elías, N. Perea-Lopez, J. Suhr, ACS Nano 2014, 8, 5959.
- [87] J. Cao, Y. Zhang, C. Men, Y. Sun, Z. Wang, X. Zhang, Q. Li, ACS Nano 2014, 8, 4325.
- [88] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, Sci. Rep. 2012, 2, 613.
- [89] G. Huang, C. Hou, Y. Shao, H. Wang, Q. Zhang, Y. Li, M. Zhu, Sci. Rep. 2014, 4, 4248.
- [90] K. W. Putz, O. C. Compton, M. J. Palmeri, S. T. Nguyen, L. C. Brinson, Adv. Funct. Mater. 2010, 20, 3322.
- [91] Y.-Q. Li, T. Yu, T.-Y. Yang, L.-X. Zheng, K. Liao, Adv. Mater. 2012, 24, 3426.
- [92] S. Wan, J. Peng, Y. Li, H. Hu, L. Jiang, Q. Cheng, ACS Nano 2015, 9, 9830.
- [93] A. Mirabedini, J. Foroughi, B. Thompson, G. G. Wallace, Adv. Eng. Mater. 2016. 18, 284.
- [94] S. Wan, H. Hu, J. Peng, Y. Li, Y. Fan, L. Jiang, Q. Cheng, Nanoscale 2016, 8, 5649.
- [95] C.-H. Zhu, Y. Lu, J. Peng, J.-F. Chen, S.-H. Yu, Adv. Funct. Mater. 2012, 22, 4017.
- [96] N. V. Medhekar, A. Ramasubramaniam, R. S. Ruoff, V. B. Shenoy, ACS Nano 2010, 4, 2300.
- [97] O. C. Compton, S. W. Cranford, K. W. Putz, Z. An, L. C. Brinson, M. J. Buehler, S. T. Nguyen, ACS Nano 2012, 6, 2008.
- [98] S. M. Lee, E. Pippel, U. Gosele, C. Dresbach, Y. Qin, C. V. Chandran, T. Brauniger, G. Hause, M. Knez, *Science* 2009, *324*, 488.
- [99] X. Hu, Z. Xu, C. Gao, Sci. Rep. 2012, 2, 767.
- [100] Z. Xu, C. Gao, Nat. Commun. 2011, 2, 571.
- [101] K. Hu, L. S. Tolentino, D. D. Kulkarni, C. Ye, S. Kumar, V. V. Tsukruk, Angew. Chem. Int. Ed. 2013, 52, 13784.
- [102] G. W. Bryan, P. E. Gibbs, J. Mar. Biol. Assoc. UK 1979, 59, 969.
- [103] P. E. Gibbs, G. W. Bryan, J. Mar. Biol. Assoc. UK 1980, 60, 205.
- [104] S. Park, K.-S. Lee, G. Bozoklu, W. Cai, S. T. Nguyen, R. S. Ruoff, ACS Nano 2008, 2, 572.

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- [105] X. Jiang, Y. Ma, J. Li, Q. Fan, W. Huang, J. Phys. Chem. C 2010, 114, 22462.
- [106] D. V. Lam, T. Gong, S. Won, J. H. Kim, H. J. Lee, C. Lee, S. M. Lee, *Chem. Commun.* 2015, *51*, 2671.
- [107] C.-N. Yeh, K. Raidongia, J. Shao, Q.-H. Yang, J. Huang, Nat. Chem. 2015, 7, 166.
- [108] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, J. Am. Chem. Soc. 2008, 130, 5856.
- [109] Y. Liu, L. Yuan, M. Yang, Y. Zheng, L. Li, L. Gao, N. Nerngchamnong, C. T. Nai, C. S. S. Sangeeth, Y. P. Feng, C. A. Nijhuis, K. P. Loh, *Nat. Commun.* **2014**, *5*, 5461.
- [110] A. J. Patil, J. L. Vickery, T. B. Scott, S. Mann, Adv. Mater. 2009, 21, 3159.
- [111] J. Zhang, Y. Xu, L. Cui, A. Fu, W. Yang, C. Barrow, J. Liu, Compos. Part. A-Appl. S 2015, 71, 1.
- [112] C.-C. Teng, C.-C. M. Ma, C.-H. Lu, S.-Y. Yang, S.-H. Lee, M.-C. Hsiao, M.-Y. Yen, K.-C. Chiou, T.-M. Lee, *Carbon* 2011, 49, 5107.
- [113] S. Park, D. A. Dikin, S. T. Nguyen, R. S. Ruoff, J. Phys. Chem. C 2009, 113, 15801.
- [114] Y. Gao, L.-Q. Liu, S.-Z. Zu, K. Peng, D. Zhou, B.-H. Han, Z. Zhang, ACS Nano 2011, 5, 2134.
- [115] Y. S. Kim, J. H. Kang, T. Kim, Y. Jung, K. Lee, J. Y. Oh, J. Park, C. R. Park, Chem. Mater. 2014, 26, 5549.
- [116] M. A. O'Neill, S. Eberhard, P. Albersheim, A. G. Darvill, *Science* 2001, 294, 846.
- [117] Z. An, O. C. Compton, K. W. Putz, L. C. Brinson, S. T. Nguyen, Adv. Mater. 2011, 23, 3842.
- [118] L. Q. Liu, Y. Gao, Q. Liu, J. Kuang, D. Zhou, S. T. Ju, B. H. Han, Z. Zhang, Small 2013, 9, 2466.
- [119] Q. Cheng, M. Wu, M. Li, L. Jiang, Z. Tang, Angew. Chem. Int. Ed. 2013, 52, 3750.
- [120] Y. Tian, Y. Cao, Y. Wang, W. Yang, J. Feng, Adv. Mater. 2013, 25, 2980.
- [121] Z. Jia, Y. Wang, J. Mater. Chem. A 2015, 3, 4405.
- [122] S. Gong, W. Cui, Q. Zhang, A. Cao, L. Jiang, Q. Cheng, ACS Nano 2015, 9, 11568.
- [123] X. Z. Hu, Z. Xu, Z. Liu, C. Gao, Sci. Rep. 2013, 3, 2374.
- [124] L. Kou, C. Gao, Nanoscale **2013**, *5*, 4370.
- [125] Z. Liu, Z. Xu, X. Z. Hu, C. Gao, Macromolecules 2013, 46, 6931.
- [126] Z. Xu, H. Sun, X. Zhao, C. Gao, Adv. Mater. 2013, 25, 188.
- [127] X. L. Zhao, Z. Xu, B. N. Zheng, C. Gao, Sci. Rep. 2013, 3, 3164.
- [128] L. Kou, T. Q. Huang, B. N. Zheng, Y. Han, X. L. Zhao, K. Gopalsamy, H. Y. Sun, C. Gao, *Nat. Commun.* **2014**, *5*, 3754.
- [129] Z. Liu, Z. Li, Z. Xu, Z. X. Xia, X. Z. Hu, L. Kou, L. Peng, Y. Y. Wei, C. Gao, *Chem. Mater.* **2014**, *26*, 6786.
- [130] Z. Xu, C. Gao, Acc. Chem. Res. 2014, 47, 1267.
- [131] F. Meng, W. Lu, Q. Li, J.-H. Byun, Y. Oh, T.-W. Chou, Adv. Mater. 2015, 27, 5113.
- [132] L. Peng, Z. Xu, Z. Liu, Y. Y. Wei, H. Y. Sun, Z. Li, X. L. Zhao, C. Gao, *Nat. Commun.* **2015**, *6*, 5716.
- [133] Z. Xu, C. Gao, Mater. Today 2015, 18, 480.
- [134] X. Hu, S. Rajendran, Y. Yao, Z. Liu, K. Gopalsamy, L. Peng, C. Gao, Nano Res. 2016, 1, 1.
- [135] Y. Zhang, Y. Li, P. Ming, Q. Zhang, T. Liu, L. Jiang, Q. Cheng, Adv. Mater. 2016, 28, 2834.
- [136] W. D. Zhang, I. Y. Phang, T. X. Liu, Adv. Mater. 2006, 18, 73.
- [137] K. E. Prasad, B. Das, U. Maitra, U. Ramamurty, C. N. R. Rao, Proc. Natl. Acad. Sci. USA 2009, 106, 13186.
- [138] M. K. Shin, B. Lee, S. H. Kim, J. A. Lee, G. M. Spinks, S. Gambhir, G. G. Wallace, M. E. Kozlov, R. H. Baughman, S. J. Kim, *Nat. Commun.* 2012, 3, 650.
- [139] R. Jalili, S. H. Aboutalebi, D. Esrafilzadeh, K. Konstantinov, S. E. Moulton, J. M. Razal, G. G. Wallace, ACS Nano 2013, 7, 3981.
- [140] X. Huang, Z. Y. Zeng, H. Zhang, Chem. Soc. Rev. 2013, 42, 1934.

- [141] S. Bertolazzi, J. Brivio, A. Kis, ACS Nano 2011, 5, 9703.
- [142] S. Wan, Y. Li, J. Peng, H. Hu, Q. Cheng, L. Jiang, ACS Nano 2015, 9, 708.
- [143] B. Fang, L. Peng, Z. Xu, C. Gao, ACS Nano 2015, 9, 5214.
- [144] P. Ming, Z. Song, S. Gong, Y. Zhang, J. Duan, Q. Zhang, L. Jiang, Q. Cheng, J. Mater. Chem. A 2015, 3, 21194.
- [145] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, Adv. Mater. 2012, 24, 5979.
- [146] Y. Xu, G. Long, L. Huang, Y. Huang, X. Wan, Y. Ma, Y. Chen, *Carbon* 2010, 48, 3308.
- [147] Z. Yin, S. Sun, T. Salim, S. Wu, X. Huang, Q. He, Y. M. Lam, H. Zhang, ACS Nano 2010, 4, 5263.
- [148] E. Kymakis, K. Savva, M. M. Stylianakis, C. Fotakis, E. Stratakis, *Adv. Funct. Mater.* **2013**, *23*, 2742.
- [149] L. Gomez De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson, C. Zhou, ACS Nano 2010, 4, 2865.
- [150] Y. Zhu, Z. Sun, Z. Yan, Z. Jin, J. M. Tour, ACS Nano 2011, 5, 6472.
- [151] Y. H. Kahng, M.-K. Kim, J.-H. Lee, Y. J. Kim, N. Kim, D.-W. Park, K. Lee, Sol. Energy Mater. Sol. Cells 2014, 124, 86.
- [152] Z. Liu, Q. Liu, Y. Huang, Y. Ma, S. Yin, X. Zhang, W. Sun, Y. Chen, *Adv. Mater.* 2008, 20, 3924.
- [153] H. Kim, S. H. Bae, T. H. Han, K. G. Lim, J. H. Ahn, T. W. Lee, *Nanotechnology* **2014**, *25*, 014012.
- [154] D. S. Yu, Y. Yang, M. Durstock, J. B. Baek, L. M. Dai, ACS Nano 2010, 4, 5633.
- [155] X. Ou, L. Jiang, P. Chen, M. Zhu, W. Hu, M. Liu, J. Zhu, H. Ju, Adv. Funct. Mater. 2013, 23, 2422.
- [156] C. Wu, J. Feng, L. Peng, Y. Ni, H. Liang, L. He, Y. Xie, J. Mater. Chem. 2011, 21, 18584.
- [157] G. W. Rogers, J. Z. Liu, J. Am. Chem. Soc. 2012, 134, 1250.
- [158] G. Sun, Y. Pan, Z. Zhan, L. Zheng, J. Lu, J. H. L. Pang, L. Li, W. Huang, J. Phys. Chem. C 2011, 115, 23741.
- [159] K.-Y. Shin, J.-Y. Hong, J. Jang, Chem. Commun. 2011, 47, 8527.
- [160] N. Zhang, R. Li, L. Zhang, H. Chen, W. Wang, Y. Liu, T. Wu, X. Wang, W. Wang, Y. Li, Y. Zhao, J. Gao, *Soft Matter* **2011**, *7*, 7231.
- [161] S. Park, J. An, J. W. Suk, R. S. Ruoff, Small 2010, 6, 210.
- [162] H. Cheng, Y. Hu, F. Zhao, Z. Dong, Y. Wang, N. Chen, Z. Zhang, L. Qu, Adv. Mater. 2014, 26, 2909.
- [163] H. Cheng, J. Liu, Y. Zhao, C. Hu, Z. Zhang, N. Chen, L. Jiang, L. Qu, Angew. Chem. Int. Ed. 2013, 52, 10482.
- [164] J. Zhu, C. M. Andres, J. Xu, A. Ramamoorthy, T. Tsotsis, N. A. Kotov, ACS Nano 2012, 6, 8357.
- [165] J. Zang, S. Ryu, N. Pugno, Q. Wang, Q. Tu, M. J. Buehler, X. Zhao, *Nat. Mater.* 2013, *12*, 321.
- [166] Y. Yang, W. Zhan, R. Peng, C. He, X. Pang, D. Shi, T. Jiang, Z. Lin, *Adv. Mater.* 2015, 27, 6376.
- [167] J. H. Zou, J. H. Liu, A. S. Karakoti, A. Kumar, D. Joung, Q. A. Li, S. I. Khondaker, S. Seal, L. Zhai, ACS Nano 2010, 4, 7293.
- [168] F. R. Fan, W. Tang, Z. L. Wang, Adv. Mater. 2016, 28, 4283.
- [169] R. Md Ataur, L. Byung-Chul, P. Duy-Thach, C. Gwiy-Sang, Smart Mater. Struct. 2013, 22, 085017.
- [170] J.-H. Lee, K. Y. Lee, B. Kumar, N. T. Tien, N.-E. Lee, S.-W. Kim, Energy Environ. Sci. 2013, 6, 169.
- [171] J.-H. Lee, K. Y. Lee, M. K. Gupta, T. Y. Kim, D.-Y. Lee, J. Oh, C. Ryu,
 W. J. Yoo, C.-Y. Kang, S.-J. Yoon, J.-B. Yoo, S.-W. Kim, *Adv. Mater.* 2014, *26*, 765.
- [172] W. Guo, C. Cheng, Y. Wu, Y. Jiang, J. Gao, D. Li, L. Jiang, Adv. Mater. 2013, 25, 6064.
- [173] X. Peng, L. Peng, C. Wu, Y. Xie, Chem. Soc. Rev. 2014, 43, 3303.
- [174] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, ACS Nano 2010, 4, 1963.
- [175] D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G. Q. Lu, H.-M. Cheng, ACS Nano 2009, 3, 1745.
- [176] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, Nat. Nanotechnol. 2008, 3, 101.





- [177] X. Yang, L. Qiu, C. Cheng, Y. Wu, Z.-F. Ma, D. Li, Angew. Chem. Int. Ed. 2011, 50, 7325.
- [178] X. Yang, J. Zhu, L. Qiu, D. Li, Adv. Mater. 2011, 23, 2833.
- [179] C. Wang, D. Li, C. O. Too, G. G. Wallace, Chem. Mater. 2009, 21, 2604.
- [180] X. W. Yang, C. Cheng, Y. F. Wang, L. Qiu, D. Li, Science 2013, 341, 534.
- [181] T. Huang, B. Zheng, Z. Liu, L. Kou, C. Gao, J. Mater. Chem. A 2015, 3, 1890.
- [182] L. Kou, Z. Liu, T. Q. Huang, B. N. Zheng, Z. Y. Tian, Z. S. Deng, C. Gao, *Nanoscale* **2015**, *7*, 4080.
- [183] K. Gopalsamy, Z. Xu, B. Zheng, T. Huang, L. Kou, X. Zhao, C. Gao, *Nanoscale* **2014**, 6, 8595.

- [184] B. Zheng, T. Huang, L. Kou, X. Zhao, K. Gopalsamy, C. Gao, J. Mater. Chem. A 2014, 2, 9736.
- S. H. Aboutalebi, R. Jalili, D. Esrafilzadeh, M. Salari,
 Z. Gholamvand, S. Aminorroaya Yamini, K. Konstantinov,
 R. L. Shepherd, J. Chen, S. E. Moulton, ACS Nano 2014, 8, 2456.
- [186] G. Qu, J. Cheng, X. Li, D. Yuan, P. Chen, X. Chen, B. Wang, H. Peng, Adv. Mater. 2016, 28, 3646.
- [187] G. Sun, J. Liu, X. Zhang, X. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, Angew. Chem. Int. Ed. 2014, 53, 12784.
- [188] R. Jalili, S. H. Aboutalebi, D. Esrafilzadeh, R. L. Shepherd, J. Chen, S. Aminorroaya-Yamini, K. Konstantinov, A. I. Minett, J. M. Razal, G. G. Wallace, *Adv. Funct. Mater.* **2013**, *23*, 5345.
- [189] Z. Xu, Z. Liu, H. Sun, C. Gao, Adv. Mater. 2013, 25, 3249.