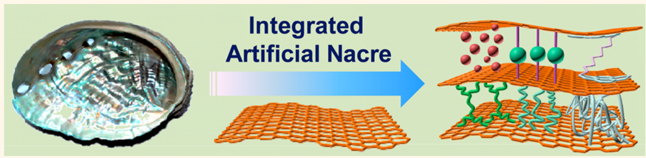
Learning from Nature: Constructing Integrated Graphene-Based Artificial Nacre

Qunfeng Cheng,* Jianli Duan, Qi Zhang, and Lei Jiang

Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, BeiHang University, Beijing 100191, P. R. China

ABSTRACT Natural nacre supplies a number of properties that can be used in designing high-performance bioinspired materials. Likewise, due to the extraordinary properties of graphene, a series of bioinspired graphene-based materials have recently been demonstrated. Compared to other approaches for constructing graphene-based materials, bioinspired concepts result in high-loading graphene, and the resultant high-performance graphene-based artificial nacres demonstrate isotropic mechanical and electrical properties. In this Perspective, we describe how to construct integrated graphene-based artificial nacre through the synergistic relationship between interface interactions and building blocks. These integrated graphene-based artificial nacres show promising applications in many fields, such as aerospace, flexible supercapacitor electrodes, artificial muscle, and tissue engineering.



KEYWORDS: nacre · graphene · bioinspired · integrated materials

Over billions of years, intricately structured, high-performance natural materials, such as nacre (also known as mother of pearl), have evolved.[1] Nacre has several properties that have been a source of inspiration for biomimetic materials: (a) a "brick and mortar" layered architecture alternatively packed with 95 vol % of two-dimensional (2D) aragonite calcium carbonate platelets, and 5 vol % of one-dimensional (1D) nanofibrillar chitin and protein, and (b) different interface interactions between inorganic platelets and organic protein.[1] In fact, the extraordinary properties of natural nacre are attributed to the synergistic toughening effects from the different building blocks and interface interactions, as shown in Figure 1. A series of high-performance bioinspired layered materials have been successfully demonstrated, including montmorillonite (MTM)–poly(vinyl alcohol) (PVA) by layer-by-layer (LBL),[2] Al_2O_3–Chitosan by spin coating,[3] and Al_2O_3–poly(methyl methacrylate) (PMMA) by ice-templating.[4] However, optimization of the tensile strength often comes at the expense of toughness,[5] which means that it remains a great challenge to improve tensile strength and toughness simultaneously in order to obtain integrated bioinspired layered materials. Graphene oxide (GO),[6] a water-soluble derivative of graphene with many functional groups on the surface, is one of the best candidates for fabricating bioinspired layered materials, because functional surface groups enable interface designs that can improve the interfacial strength in composites.

Synergistic Interfacial Interactions. Typical interface categories of graphene-based artificial nacre are hydrogen bonds, ionic bonds, $\pi-\pi$ interactions, and covalent bonding.[7] Some high mechanical performance graphene-based artificial nacres have been achieved through construction of these interfacial interactions. For example, An *et al.*[8] demonstrated ultrastiff artificial nacre through borate orthoester covalent bonding between GO nanosheets (GO–borate). By The introduction of only 0.94 wt % borate ions into adjacent GO nanosheets, borate oligo-orthoesters are formed with GO nanosheets through hydroxyl moieties on the GO surface. The storage modulus of GO–borate artificial nacre reached 127 GPa from 30 GPa for the pure GO film. However, the strain of GO–borate artificial nacre is only 0.15%, and the toughness is low at 0.14 $MJ \cdot m^{-3}$, which is lower than $^{1}/_{10}$ of natural nacre's

* Address correspondence to cheng@buaa.edu.cn.

Published online March 12, 2015
10.1021/acsnano.5b01126

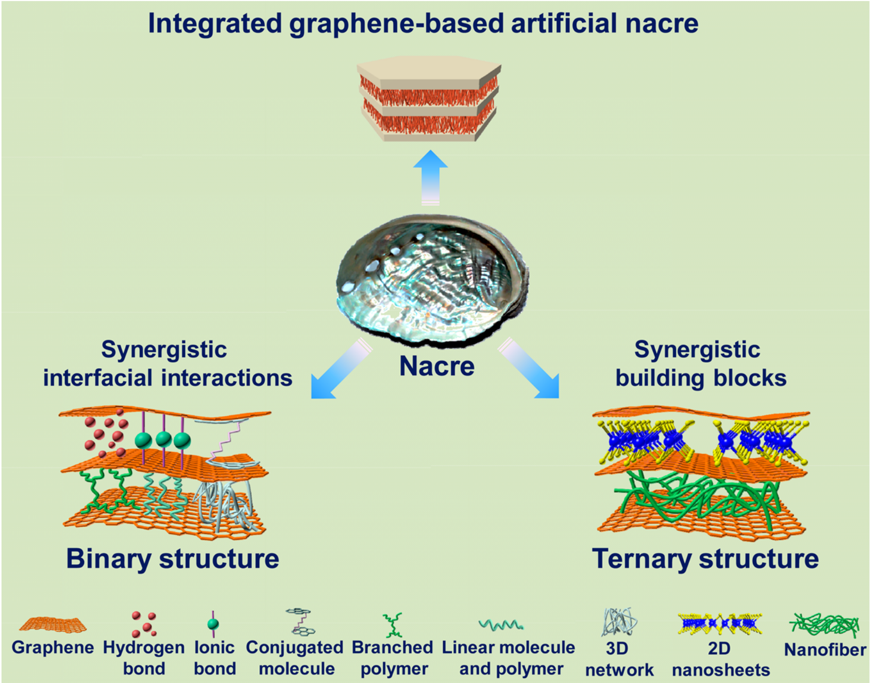


Figure 1. Integrated graphene-based artificial nacre: (a) Natural nacre with a typical micro/nanoscale hierarchical structure supplies the concept for constructing high-performance bioinspired materials. Graphene oxide (GO), with its outstanding physical properties, is one of the best candidates for fabricating bioinspired layered materials. Their many functional surface groups enable interface designs that improve the interfacial strength in the resultant bioinspired composites. Bottom left: The synergistic interfacial interaction is one important approach for constructing integrated graphene-based artificial nacre. Several typical interfacial interactions include hydrogen bonding, ionic bonding, $\pi-\pi$ interactions, branched polymers, linear molecules and polymers, and three-dimensional (3D) thermosetting resin networks. Bottom right: The use of synergistic building blocks is another way to construct integrated artificial nacre. The other building blocks could be two 2D nanosheets, such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), or 1D nanofibers, such as carbon nanotubes (CNT) and nanofibrillar cellulose (NFC). We expect that a breakthrough in graphene-based artificial nacre will be developed through a combination of the synergistic effects of interfacial interactions and building blocks.

toughness (1.8 $MJ \cdot m^{-3}$).[9] Tian *et al.*[10] demonstrated high-strength artificial nacre through covalent bonding between polydopamine (PDA)-modified GO nanosheets and poly(ether imide) (PEI) polymers. The Young's modulus reaches 103.4 GPa, and the tensile strength is as high as 209.9 MPa. However, the elongation dramatically decreases to only 0.22%, and the toughness is only 0.23 $MJ \cdot m^{-3}$, which is only one-eighth of natural nacre's toughness (1.8 $MJ \cdot m^{-3}$).[9]

Is it possible to achieve integrated high strength and toughness simultaneously for graphene-based artificial nacre? Yes, and, in fact, natural nacre has demonstrated a promising solution known as the synergistic effect, which comes from interface interactions, such as different interface interactions and bridges, or building blocks, including $CaCO_3$ platelets and chitin nanofibers.[1] As shown in Figure 1 (bottom left), synergistic interfacial interactions have been demonstrated in the binary structure of graphene-based artificial nacre. We successfully adopted a long linear chain of molecules, 10,12-pentacosadiyn-1-ol (PCDO),[11] for constructing a synergistic interface interaction with hydrogen bonds and covalent bonds between the GO nanosheets in the resultant bioinspired layered materials. When loading, the reduced GO nanosheets extensively slide against each other. The weak hydrogen bonds are first ruptured, and the coiled PCDO molecules are stretched along the sliding direction, resulting in the dissipation of a large amount of energy. When further increasing the loading force, the chemical bonds between the PCDO molecules and the reduced GO nanosheets are broken, simultaneously resulting in the curving of the reduced GO nanosheets. The tensile strength and toughness reach 129.6 MPa and 3.91 $MJ \cdot m^{-3}$, respectively. Hu *et al.*[12] also demonstrated the high tensile strength of GO–silk fibroin (GO–SL) layered materials with 300 MPa and 2.8 $MJ \cdot m^{-3}$ through synergistic hydrogen bonds and cross-linking bonds, reducing the slippage ability of silk backbones. We have also

> The extraordinary properties of natural nacre are attributed to the synergistic toughening effects from the different building blocks and interface interactions.

demonstrated the integrated high strength and toughness of artificial nacre based on GO–poly(dopamine) formed through synergistic hydrogen and covalent bonds, with the strength and toughness reaching 204.9 MPa and 4.0 MJ·m^{-3}, respectively. Recently, Zhang *et al.*[13] fabricated reduced GO materials with ultrahigh strength and toughness with poly(acrylic acid-*co*-(4-acrylamidophenyl)boronic acid) (PAPB), which interacts extremely well with GO nanosheets. For example, PAPB forms synergistic interactions between hydrogen bonds and $\pi-\pi$ interactions, which interlock intimately with GO nanosheets into well-layered structures. Additionally, PAPB not only increases the strain at break, but also provides more interfacial areas available for stress transfer between GO layers, resulting in ultrahigh strength and toughness as well as high electrical conductivity. The tensile strength (382 MPa) and toughness (7.5 MJ·m^{-3}) reach two and four times higher than those of natural nacre,[9] respectively.

Is it possible to achieve integrated high strength and toughness simultaneously for graphene-based artificial nacre?

Synergistic Building Blocks. The other approach for achieving integrated graphene-based artificial nacre is constructing a ternary structure, which is inspired by the nacre structure with 2D aragonite calcium carbonate platelets and 1D nanofibrillar chitin, as shown in Figure 1 (bottom right). Two different building blocks will form a synergistic effect to improve the strength and toughness simultaneously.[14,15] For example, we have demonstrated an integrated ternary artificial nacre through the synergistic toughening of nanoclay, nanofibrillar cellulose, and poly(vinyl alcohol),[16] and graphene oxide (GO)–molybdenumdisulfide (MoS_2)–thermoplastic polyurethane (TPU),[17] respectively. The synergistic toughening effect from the strength of GO and the lubricant properties of MoS_2 has been successfully revealed and demonstrated by optimizing the ratio of GO to MoS_2 in the ternary structure. The tensile strength (235 MPa) and toughness (6.9 MJ·m^{-3}) are simultaneously improved, reach 1.7 and 3.8 times higher than those of natural nacre,[9] respectively, and are superior to other common binary graphene-based materials. Compared to synergistic interfacial interactions in the binary structure, the synergistic building blocks in the ternary structure show two advantages: (a) the synergistic effect can be quantifiably optimized by adjusting the ratio of two building blocks, and (b) the interface in the ternary structure can be also designed into different interactions with building blocks.

Although research on artificial nacre first started more than 20 years ago, integrated graphene-based artificial nacre is still in its early stages. Work in this area would be greatly enhanced by the synergistic effects of designing interface interactions and combining different building blocks. In our research, we have demonstrated an integrated graphene-based artificial nacre with isotropic mechanical and electrical properties due to graphene's intrinsic 2D structure, which is superior to nanofiber-reinforced composites. We therefore anticipate near-term breakthroughs in graphene-based artificial nacre for the development of promising applications in many fields, such as aerospace, flexible supercapacitor electrodes, artificial muscles, and tissue engineering. Integrated graphene-based artificial nacre may also be a potential platform for the design and construction of robust intelligent devices,[18,19] such as actuators,[20] artificial muscles,[21] and sensors.[22]

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (21273017, 51103004), the National Research Fund for Fundamental Key Projects (2010CB934700), Program for New Century Excellent Talents in University (NCET-12-0034), Beijing Nova Program (Z121103002512020), Beijing Science and Technology Program (Z121100001312004), Fok Ying-Tong Education Foundation (141045), Open Project of Beijing National Laboratory for Molecular Sciences and the 111 Project (B14009), and the Fundamental Research Funds for the Central Universities (YWF-14-HXXY-018).

REFERENCES AND NOTES

1. Wegst, U. G. K.; Bai, H.; Saiz, E.; Tomsia, A. P.; Ritchie, R. O. Bioinspired Structural Materials. *Nat. Mater.* **2015**, *14* (1), 23–36.
2. Podsiadlo, P.; Kaushik, A. K.; Arruda, E. M.; Waas, A. M.; Shim, B. S.; Xu, J.; Nandivada, H.; Pumplin, B. G.; Lahann, J.; Ramamoorthy, A.; Kotov, N. A. Ultrastrong and Stiff Layered Polymer Nanocomposites. *Science* **2007**, *318* (5847), 80–83.
3. Bonderer, L. J.; Studart, A. R.; Gauckler, L. J. Bioinspired Design and Assembly of Platelet Reinforced Polymer Films. *Science* **2008**, *319* (5866), 1069–1073.
4. Munch, E.; Launey, M. E.; Alsem, D. H.; Saiz, E.; Tomsia, A. P.; Ritchie, R. O. Tough, Bio-Inspired Hybrid Materials. *Science* **2008**, *322* (5907), 1516–1520.
5. Ritchie, R. O. The Conflicts between Strength and Toughness. *Nat. Mater.* **2011**, *10* (11), 817–822.
6. Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. Preparation and Characterization of Graphene Oxide Paper. *Nature* **2007**, *448* (7152), 457–460.
7. Cheng, Q.; Jiang, L.; Tang, Z. Bioinspired Layered Materials with Superior Mechanical Performance. *Acc. Chem. Res.* **2014**, *47* (4), 1256–1266.
8. An, Z.; Compton, O. C.; Putz, K. W.; Brinson, L. C.; Nguyen, S. T. Bio-Inspired Borate Cross-Linking in Ultra-Stiff Graphene Oxide Thin Films. *Adv. Mater.* **2011**, *23* (33), 3842–3846.
9. Jackson, A.; Vincent, J.; Turner, R. The Mechanical Design of Nacre. *Proc. R. Soc. London, Ser. B* **1988**, *234* (1277), 415–440.
10. Tian, Y.; Cao, Y.; Wang, Y.; Yang, W.; Feng, J. Realizing Ultrahigh Modulus and High Strength of Macroscopic Graphene Oxide Papers Through Crosslinking of Mussel-Inspired Polymers. *Adv. Mater.* **2013**, *25* (21), 2980–2983.
11. Cheng, Q.; Wu, M.; Li, M.; Jiang, L.; Tang, Z. Ultratough Artificial Nacre Based on Conjugated Cross-Linked Graphene Oxide. *Angew. Chem., Int. Ed.* **2013**, *52* (13), 3750–3755.

12. Hu, K.; Tolentino, L. S.; Kulkarni, D. D.; Ye, C.; Kumar, S.; Tsukruk, V. V. Written-in Conductive Patterns on Robust Graphene Oxide Biopaper by Electrochemical Microstamping. *Angew. Chem., Int. Ed.* **2013**, *52* (51), 13784–13788.
13. Zhang, M.; Huang, L.; Chen, J.; Li, C.; Shi, G. Ultratough, Ultrastrong, and Highly Conductive Graphene Films with Arbitrary Sizes. *Adv. Mater.* **2014**, *26* (45), 7588–7592.
14. Prasad, K. E.; Das, B.; Maitra, U.; Ramamurty, U.; Rao, C. N. R. Extraordinary Synergy in the Mechanical Properties of Polymer Matrix Composites Reinforced with 2 Nanocarbons. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (32), 13186–13189.
15. Shin, M. K.; Lee, B.; Kim, S. H.; Lee, J. A.; Spinks, G. M.; Gambhir, S.; Wallace, G. G.; Kozlov, M. E.; Baughman, R. H.; Kim, S. J., Synergistic Toughening of Composite Fibres by Self-Alignment of Reduced Graphene Oxide and Carbon Nanotubes. *Nat. Commun.* **2012**, *3*.
16. Wang, J.; Cheng, Q.; Lin, L.; Jiang, L. Synergistic Toughening of Bioinspired Poly(vinyl alcohol)−Clay−Nanofibrillar Cellulose Artificial Nacre. *ACS Nano* **2014**, *8* (3), 2739–2745.
17. Wan, S.; Li, Y.; Peng, J.; Hu, H.; Cheng, Q.; Jiang, L. Synergistic Toughening of Graphene Oxide−Molybdenum Disulfide−Thermoplastic Polyurethane Ternary Artificial Nacre. *ACS Nano* **2015**, *9* (1), 708–714.
18. Zhao, Y.; Song, L.; Zhang, Z. P.; Qu, L. T. Stimulus-Responsive Graphene Systems Towards Actuator Applications. *Environ. Eng. Sci.* **2013**, *6* (12), 3520–3536.
19. Zhang, J.; Song, L.; Zhang, Z. P.; Chen, N.; Qu, L. T. Environmentally Responsive Graphene Systems. *Small* **2014**, *10* (11), 2151–2164.
20. Liang, J.; Huang, L.; Li, N.; Huang, Y.; Wu, Y.; Fang, S.; Oh, J.; Kozlov, M.; Ma, Y.; Li, F.; Baughman, R.; Chen, Y. Electromechanical Actuator with Controllable Motion, Fast Response Rate, and High-Frequency Resonance Based on Graphene and Polydiacetylene. *ACS Nano* **2012**, *6* (5), 4508–4519.
21. Zang, J. F.; Ryu, S.; Pugno, N.; Wang, Q. M.; Tu, Q.; Buehler, M. J.; Zhao, X. H. Multifunctionality and Control of the Crumpling and Unfolding of Large-Area Graphene. *Nat. Mater.* **2013**, *12* (4), 321–325.
22. Zhu, J.; Andres, C. M.; Xu, J.; Ramamoorthy, A.; Tsotsis, T.; Kotov, N. A. Pseudonegative Thermal Expansion and the State of Water in Graphene Oxide Layered Assemblies. *ACS Nano* **2012**, *6* (9), 8357–8365.