ACS APPLIED MATERIALS & INTERFACES
Research Article
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Bioinspired Hierarchical Alumina−Graphene Oxide−Poly(vinyl alcohol) Artificial Nacre with Optimized Strength and Toughness

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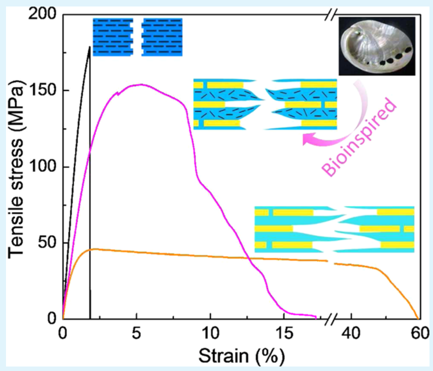
Ⓢ *Supporting Information*

ABSTRACT: Due to hierarchical organization of micro- and nanostructures, natural nacre exhibits extraordinary strength and toughness, and thus provides a superior model for the design and fabrication of high-performance artificial composite materials. Although great progress has been made in constructing layered composites by alternately stacking hard inorganic platelets and soft polymers, the real issue is that the excellent strength of these composites was obtained at the sacrifice of toughness. In this work, inspired by the layered aragonite microplatelets/chitin nanofibers−protein structure of natural nacre, alumina microplatelets−graphene oxide nanosheets−poly(vinyl alcohol) (Al_2O_3/GO−PVA) artificial nacre is successfully constructed through layer-by-layer bottom-up assembly, in which Al_2O_3 and GO−PVA act as "bricks" and "mortar", respectively. The artificial nacre has hierarchical "brick-and-mortar" structure and exhibits excellent strength (143 ± 13 MPa) and toughness (9.2 ± 2.7 MJ/m^3), which are superior to those of natural nacre (80−135 MPa, 1.8 MJ/m^3). It was demonstrated that the multiscale hierarchical structure of ultrathin GO nanosheets and submicrometer-thick Al_2O_3 platelets can deal with the conflict between strength and toughness, thus leading to the excellent mechanical properties that cannot be obtained using only one size of platelet. We strongly believe that the work presented here provides a creative strategy for designing and developing new composites with excellent strength and toughness.



KEYWORDS: *bioinspiration, graphene oxide, hierarchical structure, mechanical properties, nacre*

■ INTRODUCTION

Layered composites based on two-dimensional inorganic platelets have experienced a surge interest in their unique structure and properties.[1−3] Compared to one-dimensional fibers, the orientation of lamellar structures can bear load in two directions parallel to platelets and thus provide excellent loading capacity.[4] Great efforts were therefore made to assemble the ordered layered composites by using different inorganic nanoplatelets along with various polymers,[5−15] which displayed impressive modulus and strength. For example, nanoclay-based and graphene oxide-based layered films with ultrahigh modulus and strength were reported.[14,15] The tremendous interfacial area arising from their ultralow thickness may improve stress transfer efficiency. Further chemical cross-linking between inorganic nanoplatelets and polymers dramatically increase the modulus. However, the excellent modulus and strength of these composites are usually accompanied by extremely low strain and toughness, which would cause catastrophic failure during the application process. The reason is mainly that polymers are confined in the narrow interlamellar space between ultrathin nanoplatelets, and lose original ductility and flexibility.[15,16] To address this issue, we used microplatelets instead of nanoplatelets to construct layered composites.[17−21] Bonderer et al. demonstrated that the layered material based on chitosan and submicrometer-thick alumina microplatelets showed high ductility.[21] The alumina microplatelets are thick enough to keep the ability of polymer matrix to deform and efficiently promote crack deflection, but generate inferior strength due to deterioration of load transfer efficiency.[17,18] From the viewpoint of applications, therefore, new reinforcement strategies are highly desired to circumvent the conflict between strength and toughness of layered composites.[22−28]

Multiple building blocks hierarchically arranged at different scales is a universal principle used by many natural materials to optimize their mechanical properties.[29−31] Among them, natural nacre, as an excellent example, consists of hard aragonite microplatelets, rigid chitin nanofibers and soft protein,[32−36] which shows a unique combination of remarkable strength and toughness.[37] The excellent mechanical properties are attributed to two levels of micro/nanoscale hierarchical structure. The first level is that soft protein is reinforced with a small quantity of rigid chitin nanofibers, which acts as viscoelastic compound "mortar".[38,39] The second level is that

Received: March 13, 2015
Accepted: April 13, 2015
Published: April 13, 2015

DOI: 10.1021/acsami.5b02194
ACS Appl. Mater. Interfaces 2015, 7, 9281−9286

the compound mortar is alternately stacked together with hard aragonite microplatelets to form layered "brick-and-mortar" structures, thus providing increased strength. In addition, the aragonite "bricks" greatly promote crack deflection, which increases viscoelastic energy dissipation of compound mortar and improves toughness.[40]

In this study, guided by both multiscale hierarchical structure and extraordinary mechanical properties of natural nacre, we successfully combine (Al_2O_3) microplatelets and graphene oxide (GO) nanosheets at two different scales to construct artificial nacre through layer-by-layer bottom-up colloidal assembly. The trick is that Al_2O_3 microplatelets acted as bricks, while GO nanosheets-reinforced PVA served as mortar. It is demonstrated that nacre-like hierarchical structure contributes to excellent balance of strength and toughness that could not be obtained using only one platelet size.

EXPERIMENTAL SECTION

Materials. Al_2O_3 microplatelets used in this study were acquired from Merck KGaA (Darmstadt, Germany). GO were purchased from XianFeng NANO Co., Ltd. PVA (M_w = 146 000−186 000) and 3-aminopropyltriethoxysilane (ATES) were purchased from Sigma-Aldrich.

Modification of Al_2O_3 Microplatelets. ATES (10 mL) was added into the mixture of water (75 mL) and methanol (25 mL), followed by stir for an hour to fully hydrolyze ATES. Al_2O_3 platelets (3.98 g) were then added into the hydrolyzed ATES solution and mildly sonicated for 15 min. After ultrasonication, the suspension was stirred for 30 min at 40 °C. The silylanized platelets were washed three times by centrifugation with ethanol and diluted to 1 vol % suspension in ethanol.

Fabrication of Al_2O_3/GO−PVA Film. In a typical procedure, GO (0.104 g) was dispersed by ultrasonication in deionized water (26 g). PVA (1.2 g) was dissolved in deionized water (13.8 g). The GO dispersion and PVA solution were mixed to obtain GO/PVA dispersion (GO/PVA mass ratio 8:92). The GO/PVA dispersion was drop onto a 30 × 30 mm clean glass substrate and spin coated at 600 rpm to form a flat layer of GO/PVA. Subsequently, the coated glass substrate was dried at 40 °C. The 1 vol % Al_2O_3 platelet suspension was added dropwise to a breaker with deionized water until one continuous layer of Langmuir film was formed at the air−water interface. The beaker was then sonicated for 15 min to homogenize the formed Al_2O_3 platelet monolayer. The homogeneous Al_2O_3 platelet monolayer was transferred to the GO/PVA-coated glass substrate by manual dipping and dried at 40 °C. Sequential alternate deposition of GO/PVA layer and Al_2O_3 platelet layer led to multilayered hybrid film.

Characterization. Mechanical properties were tested in the tensile mode in a universal mechanical testing machine (Shimadzu AGS-X, Japan). The tested rectangular strips were about 30 mm in length and 2 mm in width. The distance between the clamps was 5 mm and the load speed was 1 mm/min. The exact cross-section widths and thicknesses were carefully determined by scanning electron microscopy (SEM). SEM images were obtained with a field emission scanning electron microscope (JEOL, JSM-7500F). Thermogravimetric analysis (TGA) was performed on a Diamond TG/DTA thermal analyzer under air at a heating rate of 5 °C/min. Differential scanning calorimetry (DSC) was performed using a DSC 6220 (SII Nano Technology, Inc., Japan) instrument under N_2 at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

In natural nacre,[41] the diameter and thickness of aragonite platelets are approximately 8 μm and 400 nm, respectively. The chitin nanofibers with high specific area have diameter of several nanometers. The Al_2O_3 platelets used in present study have diameter of 5−12 μm and thickness of 200−500 nm, which are comparable to those of aragonite platelets (Figure 1a,b). The used GO sheets have diameter of 200−600 nm and

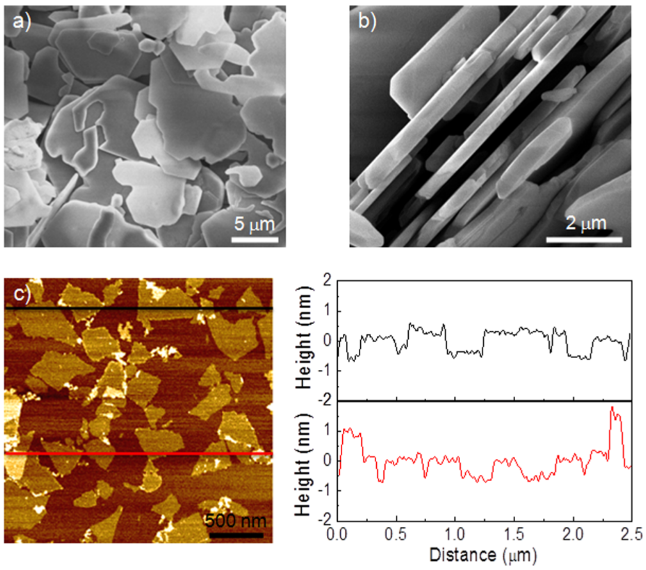


Figure 1. Morphologies of GO and Al_2O_3. (a and b) SEM images of Al_2O_3. (c, left) AFM image of GO with (right) corresponding height profiles.

thickness of about 0.65 nm (Figure 1c), which may provide tremendous specific area similar to chitin nanofibers in natural nacre. PVA is selected as a target polymer due to its high ductility and strong affinity with GO.

To determine the loading of GO in compound "mortar", GO/PVA films with different GO loading was prepared through solution casting. The dependence of their mechanical properties on GO loading is shown in Figure 2. Due to

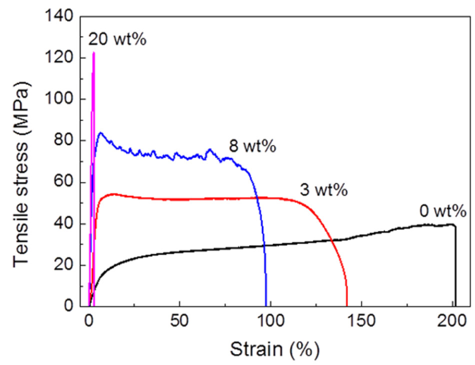


Figure 2. Representative stress−strain behavior for PVA reinforced with different GO weight loadings. The addition of 8 wt % GO leads to marked reinforcement and keeps the matrix sufficiently ductile for further incorporation of Al_2O_3 microplatelets.

tremendous specific area and strong interfacial interaction through hydrogen bond, which is proved by FTIR (Supporting Information, Figure S1),[42] GO/PVA films show obvious enhancements of mechanical properties with addition of a little GO. For example, when only 3 wt % GO was incorporated, the modulus and yield strength of GO/PVA film were improved by 5.5 times and 2.4 times, respectively. However, strain of the films sharply decreased with the increasing the GO contents due to strong restriction of PVA

DOI: 10.1021/acsami.5b02194
ACS Appl. Mater. Interfaces 2015, 7, 9281−9286

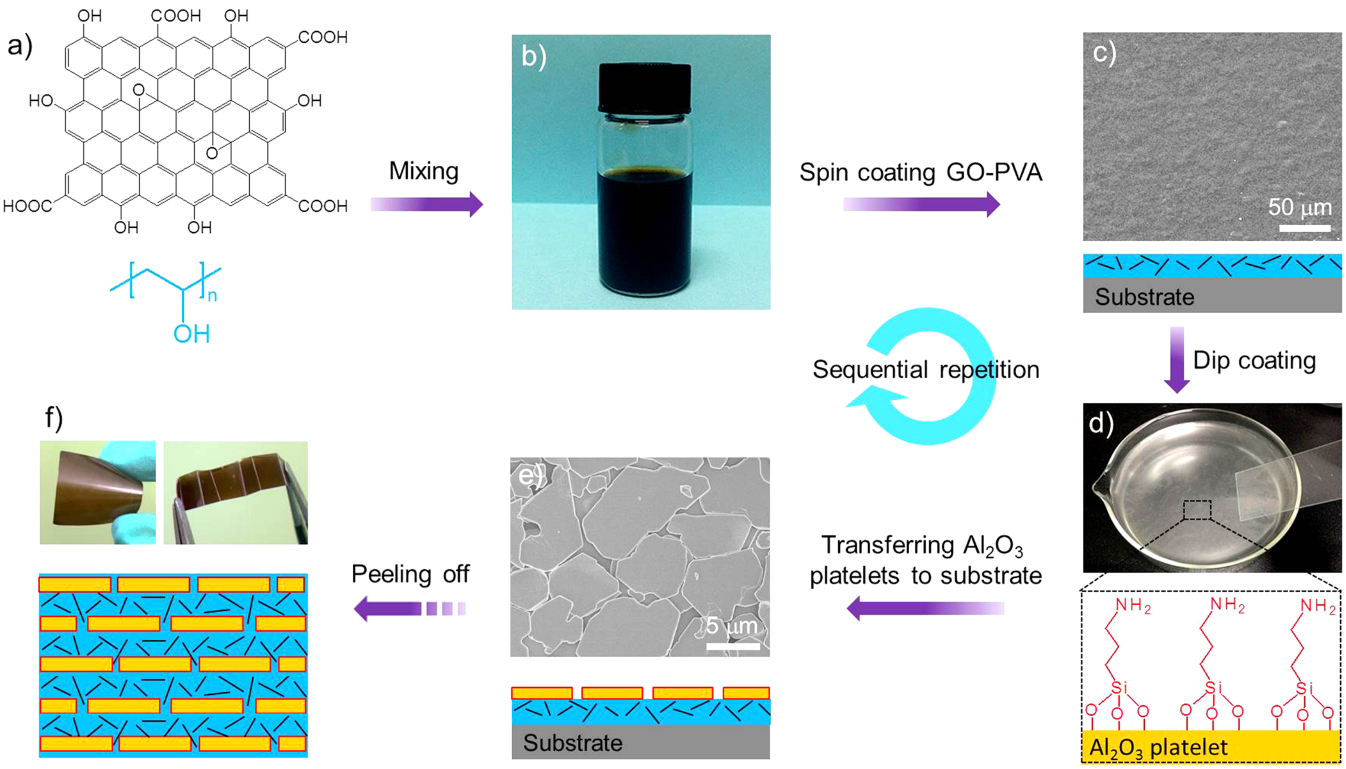


Figure 3. Layer-by-layer bottom-up assembly of multilayered Al_2O_3/GO−PVA artificial nacre. (a) GO and PVA. (b) Mixing of PVA and GO nanosheets. (c) Spin coating one layer of GO−PVA onto a glass substrate. (d) Assembling silane-modified Al_2O_3 microplatelets into monolayer at air−water interface. (e) Transferring the assembled Al_2O_3 monolayer onto GO−PVA layer. (f) The obtained flexible, foldable artificial nacre after sequential repetition.

chain motion by ultrathin nanosheets.[16] For instance, GO/PVA film with 20 wt % GO has a break strain of only 2% without any ductility. It is deducted that, therefore, the appropriate GO content in films is very critical for maintaining its strength and strain. As expected, GO/PVA compound with 8 wt % GO has reasonably high strength and sufficient ductility, and thus, it is chose as compound mortar for further constructing hierarchical artificial nacre.

Hierarchical Al_2O_3/GO−PVA artificial nacre was fabricated through layer-by-layer bottom-up colloidal assembly, as illustrated in Figure 3. The first step is to mix GO dispersion with PVA solution (GO/PVA weight ratio 8:92; Figure 3a,b). The mixed solution was spin coated onto a glass substrate to form one layer of GO−PVA (Figure 3c). To integrate Al_2O_3, we modified the platelets with silane coupling agent 3-aminopropyltriethoxysilane, which were assembled to form monolayer at the air−water interface (Figure 3d).[21] Then, the assembled Al_2O_3 monolayer was transferred onto GO−PVA-coated glass substrate by dip-coating (Figure 3e). The amine groups at the end of the silane hydrophobic tail are expected to form hydrogen bonds with the hydroxyl groups of PVA, thus increasing the interaction between microplatelets and polymer matrix. Sequential repetition of these steps leads to multilayered Al_2O_3/GO−PVA artificial nacre. The free-standing artificial nacre film is obtained by peeling it from the substrate, which is highly flexible and can be folded without fracture (Figure 3f). It is worth mentioning that the thickness of GO−PVA layer can be tuned by altering rotation speed during spin coating. We chose the rotation speed at which GO−PVA layer just covered the lower Al_2O_3 layer.

Al_2O_3 loading in artificial nacre was determined to be approximately 31 wt % by TGA (Supporting Information, Figure S2). Taking into consideration the composition of GO−PVA layer, the loading of GO is calculated to be 5.5 wt %. According to the densities of Al_2O_3 (3.98 g/cm^3), GO (2.2 g/cm^3), and PVA (1.27 g/cm^3), the total volume fraction of the two inorganic platelets is calculated to be 17 vol %. The cross-sectional microstructure of artificial nacre, after quenching in liquid nitrogen, was investigated by SEM (Figure 4a). Artificial film exhibits a nacre-like brick-and-mortar structure with the highly aligned Al_2O_3 microplatelets stacked alternatively with GO−PVA layers. The tensile modulus and yield strength of artificial nacre were measured to confirm the hierarchical reinforcement effect of GO and Al_2O_3 in a nacre-inspired

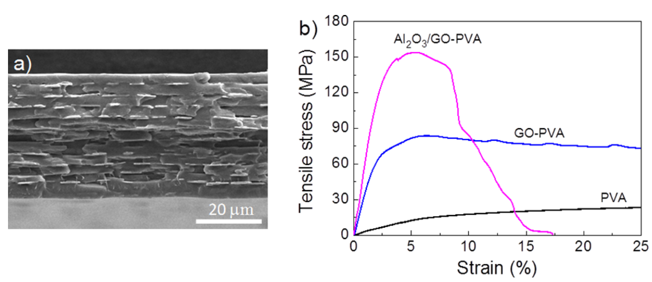


Figure 4. Microstructure and mechanical property of hierarchical Al_2O_3/GO−PVA artificial nacre. (a) Cross-sectional SEM image, showing highly oriented layered structure. (b) Comparison of mechanical property of Al_2O_3/GO−PVA artificial nacre with those of GO−PVA compound layer and PVA, indicating hierarchical reinforcement.

DOI: 10.1021/acsami.5b02194
ACS Appl. Mater. Interfaces 2015, 7, 9281−9286

layered structure (Figure 4b). As the first level of reinforcement from GO nanosheets, the yield strength of GO−PVA compound mortar sharply increases from 23 to 84 MPa, due to the GO nanosheet bonding with main chains of PVA. As the second level of reinforcement stemming from brick-and-mortar structure, a substantial fraction of tensile load can be transferred from the compound mortar to highly oriented Al_2O_3 bricks. As a result, yield strength of Al_2O_3/GO−PVA increase to 143 ± 13 MPa that is 6.2-fold higher than that of pure PVA film, and slightly higher than that of natural nacre (80−135 MPa).[43,44] Importantly, the toughness of artificial nacre reaches up to 9.2 ± 2.7 MJ/m^3, which is 5.1-fold higher than that of natural nacre (1.8 MJ/m^3).[43,44]

To confirm the reinforcement role of the hierarchical micro/nanostructure, we fabricated layered GO/PVA and Al_2O_3/PVA with the same filler volume fraction as Al_2O_3/GO−PVA artificial nacre. Layered GO/PVA was prepared through solution casting, or evaporation-induced self-assembly.[16] Layered Al_2O_3/PVA was prepared by bottom-up assembly similar to Al_2O_3/GO−PVA artificial nacre. Their tensile properties are compared in Figure 5. The Young's modulus, tensile strength, strain at break, and toughness were extracted from their stress−strain curves, as listed in Table S1 (Supporting Information). The GO/PVA film only undergoes linear elastic deformation before abrupt fracture and exhibits high strength and modulus but low strain at break without any plasticity. In contrast, the Al_2O_3/PVA shows large plastic deformation at low stress after yielding. Interestingly, Al_2O_3/GO−PVA artificial nacre simultaneously exhibits high strength and high toughness. The strength is 2.8 times higher than that of Al_2O_3/PVA, while the toughness is about 6 times higher than that of GO/PVA. The comparison of tensile test results indicates that nacre-like hierarchical structure with platelets at two different scales is beneficial to balance strength and toughness, which cannot be realized by simple layered structures composed of single microplatelets or nanoplatelets.

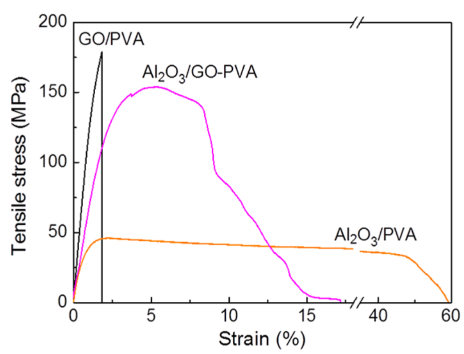


Figure 5. Comparison of mechanical property of hierarchical Al_2O_3/GO−PVA artificial nacre with those of layered GO/PVA and Al_2O_3/PVA with the same volume fraction of inorganic platelets, indicating that the nacre-like hierarchical structure helps to achieve a good balance of strength and toughness.

To clarify the mechanism of strength and toughness, we examined the fracture morphologies of layered GO/PVA, Al_2O_3/PVA, and Al_2O_3/GO−PVA artificial nacre. GO/PVA has a relatively flat fracture surface with the absence of the plastic flow of the PVA component (Figure 6a,b), implying that small size of GO nanosheets deflects crack in a limited extent. Furthermore, atom-thick GO nanosheets greatly restrict the motion of PVA molecular chains proved by DSC analysis (Supporting Information, Figure S3), thus leading to high strength and low toughness. In contrary, PVA layers in Al_2O_3/PVA film generate substantial plastic flow during the process of platelet pull-out (Figure 6c), indicating that submicrometer-thick Al_2O_3 platelets have negligible effect on the ductility of PVA layers. Under tension, the soft PVA matrix transfers load to Al_2O_3 and deforms plastically via shear.[45] The shear deformation is amplified by the staggered microstructure with large diameter of Al_2O_3 platelets, which results in large strain and energy dissipation (Figure 6d). However, thick Al_2O_3 platelets decrease load transfer efficiency, leading to low strength. For Al_2O_3/GO−PVA artificial nacre, the plastic deformation of PVA reinforced with appropriate amount of GO is basically maintained (Figure 6e). The sharp reinforcement by GO nanosheets and strain amplification by Al_2O_3 microplatelets are therefore combined (Figure 6f), which simultaneously brings about high strength and toughness. These comparisons suggest that the bioinspired hierarchical structure with the two-level reinforcement and multiscale toughening contributes to balance strength and toughness.

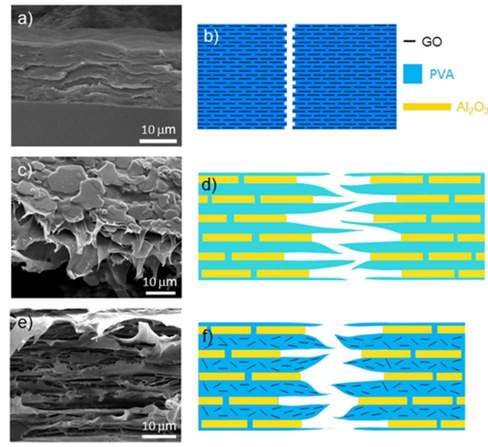


Figure 6. Fracture morphology and illustration of platelet pull-out rupture mode after tensile testing. (a and b) GO/PVA showing layered nanostructure with relatively smooth fracture surface and without plastic flow of PVA. (c and d) Al_2O_3/PVA, showing layered microstructure with rough fracture surface and large plastic elongation of PVA layers. (e and f) Al_2O_3/GO−PVA artificial nacre, showing layered hierarchical structure with rough fracture surface and appropriate plastic deformation of GO−PVA layers.

■ CONCLUSIONS

In conclusion, inspired by both the unique hierarchical structure and mechanical properties of natural nacre, Al_2O_3/GO−PVA artificial nacre was successfully fabricated through layer-by-layer bottom-up assembly. The artificial nacre has a hierarchical brick-and-mortar structure, in which PVA reinforced with ultrathin GO nanosheets serves as compound mortar and large Al_2O_3 microplatelets act as bricks. The nacre-like multiscale hierarchical structure results in excellent strength and toughness, which are superior to those of natural nacre. It is proved that the good balance of strength and toughness could not be simultaneously achieved using only one size of microplatelets or nanoplatelets. In the future, the present bioinspired hierarchical structural concept can be extended to the combination of microplatelet and nanofiber. We believe that the implementation of multiscale hierarchical layered structure would balance the strength and toughness of layered composites.

DOI: 10.1021/acsami.5b02194
ACS Appl. Mater. Interfaces 2015, 7, 9281−9286

■ ASSOCIATED CONTENT

Supporting Information

FTIR spectra, TGA curves, DSC curves, and additional experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Research Fund for Fundamental Key Projects (2012CB933200), the National Natural Science Foundation of China (51403008, 51273008, 51473008), the Fundamental Research Funds for the Central Universities (YWF-14-HHXY-008), National High Technology Research and Development Program (2012AA030305).

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DOI: 10.1021/acsami.5b02194
ACS Appl. Mater. Interfaces 2015, 7, 9281−9286