Use of Synergistic Interactions to Fabricate Strong, Tough, and Conductive Artificial Nacre Based on Graphene Oxide and Chitosan

Sijie Wan, Jingsong Peng, Yuchen Li, Han Hu, Lei Jiang, and Qunfeng Cheng*

ABSTRACT Graphene is the strongest and stiffest material, leading to the development of promising applications in many fields. However, the assembly of graphene nanosheets into macrosized nanocomposites for practical applications remains a challenge.

Nacre in its natural form sets the “gold standard” for toughness and strength, which serves as a guide to the assembly of graphene nanosheets into high-performance nanocomposites. Here we show the strong, tough, conductive artificial nacre based on graphene oxide through synergistic interactions of hydrogen and covalent bonding. Tensile strength and toughness was 4 and 10 times higher, respectively, than that of natural nacre. The exceptional integrated strong and tough artificial nacre has promising applications in aerospace, artificial muscle, and tissue engineering, especially for flexible supercapacitor electrodes due to its high electrical conductivity. The use of synergistic interactions is a strategy for the development of high-performance nanocomposites.

RESULTS AND DISCUSSION

Graphene oxide (GO) with many functional groups on its surface is an ideal candidate for the fabrication of artificial nacre. High-performance GO-based artificial nacres have been constructed through the use of different kinds of interface interactions such as ionic bonding, hydrogen bonding, covalent bonding, and π-π conjugated interactions. Although the strength and stiffness of these materials are significantly higher than those of natural nacres, GO-based artificial nacres are disadvantaged by reduced ductility or toughness. Thus, obtaining integrated strength and toughness in GO-based artificial nacre has remained a great challenge.

The extraordinary properties of natural nacre are, in fact, attributed to the synergistic toughening effects from different building blocks and interface interactions. Recently, we demonstrated integrated strength and toughness in graphene oxide-based artificial nacre through the use of synergistic building blocks: graphene oxide (GO)/molybdenum disulfide (MoS2)/thermoplastic polyurethanes (TPU).

Herein, we demonstrate the construction of integrated, strong and tough, GO-based artificial nacre through synergistic interactions of hydrogen and covalent bonding. The tensile strength and toughness of this artificial nacre reach 526.7 MPa and 17.7 MJ/m³, which is 4 and 10 times higher, respectively, than that of natural nacre. Meanwhile, the electrical conductivity of the artificial nacre was measured as high as 155.3 S/cm, which is promising for applications in aerospace, flexible supercapacitor electrodes, artificial muscle, and tissue engineering. This strategy of using synergistic interactions offers a new avenue for the development of high-performance, integrated, bioinspired nanocomposites.

KEYWORDS: artificial nacre · graphene oxide · chitosan · synergistic interaction

* Address correspondence to cheng@buaa.edu.cn.
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The fabrication of hybrid building blocks of GO-CS with high GO content is very difficult to achieve through simple mixing. That is why, until now, there have been no reports on GO-CS-based nanocomposites with high GO content. Here, we describe a simple and efficient approach developed to solve this problem. Drops of CS solution are slowly delivered into the GO solution, until a precipitate gel appears. An alkali is added to the mixing solution to adjust the charge distribution on the GO nanosheets and CS molecules. Using sonication for about 30 min, the precipitate gel is dispersed into the homogeneous suspension. With the CS content increasing, the GO nanosheets are absorbed with more CS molecules through hydrogen bonding. Intramolecular hydrogen bonding also occurs between CS molecular chains, resulting in a notable increase in the thickness of the hybrid building blocks, as confirmed by atomic force microscopy (AFM), shown in Figure S2.

X-ray diffraction (XRD) results (Figure 1a) show that the d-spacing distance increases from 8.52 Å for the pure GO film to 8.72 Å for the GO-CS-V nanocomposite (Table S2), demonstrating that the CS was successfully inserted into the GO nanosheets to form the uniform layered nacre-like structure. Additionally, the broad plateaus and multitude of peaks with 2θ values in the range 10–25° were just observed for the other GO-CS nanocomposites, indicating disordered structure of these nanocomposites. The corresponding cross-section morphology of GO-CS-based and rGO-CS nanocomposites is shown in Figures S3 and S4. The Fourier
transform infrared (FTIR) spectra (Figure 1b) show that the characteristic absorption at 1261 cm$^{-1}$, attributed to the stretch vibration of the C–N of not fully deacetylated amide groups of CS, red-shifts to 1227 cm$^{-1}$ and significantly intensifies only in the GO-CS-V composite, indicating that the amidation occurred between GO nanosheets with CS molecules. The X-ray photoelectron spectroscopy (XPS) results of the GO-CS-V nanocomposite (Figure 1c) show that the peak intensity of C–N and amide is increased and the peak intensity of protonated amine and amine groups of GO-CS-V decreases in comparison with GO-CS-E nanocomposites (Figure S5), further confirming that many more amine groups transferred into amide groups after chemical reaction in the GO-CS-V nanocomposite. The Raman spectra are shown in Figure 1d, and the corresponding $I_D/I_G$ ratios are listed in Table S3.

To further explore the chemical reaction between GO and CS in GO-CS-V nanocomposites, a mechanism of flow force effect is proposed, as shown in Figure 2. For GO-CS hybrid building blocks with low CS content, the flow force in the filtration process results in the spreading of CS molecular chains along the GO nanosheets and the formation of intermolecular hydrogen bonding between GO and CS. On the other hand, if the steric...
hindrance of CS is dramatically weakened, then the buried reaction sites (amine) distributed on the CS are exposed and chemically react with carboxyl groups on the GO nanosheets. The characteristic peak of generated amide group at 1227 cm⁻¹ appears only in the GO-CS-V nanocomposite as shown in Figure S6, which is direct evidence of covalent cross-linking between GO and the chitosan molecule. On the other hand, the covalent cross-linking could also be further confirmed by XPS, as shown in Figure 1c and Figure S5a. The XPS results of the GO-CS-V nanocomposite (Figure 1c) show that the peak intensity of the C–N and amide groups is increased and the peak intensity of protonated amine and amine groups of GO-CS-V decreases compared with the GO-CS-E nanocomposite (Figure S5a), further demonstrating that many more amine groups transferred into amide groups after chemical reaction in the GO-CS-V nanocomposite with high CS content, which decrease the friction between GO nanosheets and show low mechanical properties, especially for toughness. Detailed mechanical properties of GO-CS and rGO-CS nanocomposites are listed in Table S4.

Obviously, the high mechanical properties of rGO-CS-V artificial nacre are attributed to synergistic interactions of hydrogen and covalent bonding, which are clearly demonstrated in the stress–strain curve, as shown in Figure S7a. The cyclic loading experiments were conducted on the rGO-CS-V artificial nacre, and the stress–strain curve is shown in Figure S8. During stage I, the rGO-CS-V artificial nacre shows elastic deformation within a strain of 0.5% reversible deformation, as shown in Figure S8a. With increased loading, the plastic deformation takes place in stage II due to

![Figure 3. Stress–strain curves (a) of GO films (curve 1), rGO films (curve 2), GO-CS-V nanocomposites (curve 3), rGO-CS-V artificial nacre (curve 4), and CS films (curve 5). Tensile strength (b) and toughness (c) of the rGO-CS artificial nacre with different GO content. Proposed fracture process (d) of rGO-CS-V artificial nacre. The curled long chain of CS is gradually stretched and broken under loading, resulting in curving of the edges of the rGO nanosheets. SEM lateral view profiles of fractured surfaces of rGO films (e) and rGO-CS-V artificial nacre (f) show different fracture morphologies. Compared with the rGO films, the rGO nanosheets of rGO-CS-V artificial nacre are pulled out and curved owing to the breaking of the hydrogen and covalent bondings between rGO and CS molecules.](image_url)
and GO-Fe3⁺ and curling of GO nanosheets compared to the pure bonding is broken, leading to high fracture strength. When further increasing the loading, the covalent bonding is broken and re-formed in the slippage process, which absorbs much more energy. As loading increases during stage III, the permanent deformation reaches a larger deformation of 2.56% after successive loading—unloading cycles, as shown in Figure S8c. When further increasing the loading, the covalent bonding is broken, leading to high fracture strength and curling of GO nanosheets compared to the pure rGO film. The proposed fracture mechanism is shown in Figure 3d, and the lateral view profiles of the fracture morphology of the rGO film and rGO-CS-V artificial nacre are shown in Figure 3e and f. The fracture morphologies of the rGO film and rGO-CS-V artificial nacre are shown in Figure S9. The obvious substantial curling of reduced GO nanosheets in the rGO-CS-V artificial nacre can be observed compared to the rGO film. This mode of synergistic interactions for absorbing energy would simultaneously improve the tensile strength and toughness. The other GO-CS-based nanocomposites show only stages I and II in the stress—strain curves, as illustrated in Figure S7b, for GO-CS-I nanocomposite. As shown in Figure 4, the toughening of artificial nacre through synergistic interactions offers the advantage of integrated strength and toughness when compared with natural nacre and other GO-based nanocomposites, such as hydrogen bonding (GO-PMMA, rGO-PVA, and rGO-SL), ionic bonding (GO-Mg²⁺, GO-Ca²⁺, and GO-Fe³⁺), π–π conjugated interactions (rGO-PAPB), and covalent bonding (GO-GA, GO-borate, PGO-PEI, rGO-PCDO, and rGO-PDA). On the other hand, although the GO-CS nanocomposites with low GO content (1 wt %) show low tensile strength, the toughness is very high. The dramatic improvement of mechanical properties was ascribed to both the interaction between GO and CS and the change in crystallinity. Detailed mechanical properties of natural nacre and GO-based nanocomposites are listed in Table S5. A comparison of GO-based artificial nacre with the synergistic building blocks of rGO-MoS₂-TPU shows that synergistic interactions play a key role in improving the mechanical properties. The tensile strength and toughness of rGO-CS-V is 2.2 and 2.6 times higher, respectively, than that of rGO-MoS₂-TPU (tensile strength of 235 MPa and toughness of 6.9 MJ/m³). Furthermore, the high electrical conductivity of rGO-CS-V artificial nacre, measured at 15.5 S/cm (Table 1), is comparable with that in previously reported papers. The use of rGO-CS-V artificial nacre as a conducting wire in a circuit is demonstrated in a video (Movie S1), in which a red LED remains steadily lit while the artificial nacre is bent, indicating a potential application for it in flexible devices.

CONCLUSION

Natural nacre sets a “gold standard” for materials by having both high strength and toughness. Inspired by the natural nacre, we have fabricated artificial nacre based on graphene oxide and chitosan with almost the same ratios of inorganic and organic components in nacre, and this artificial nacre successfully integrates toughness and strength. Our finding is that the synergistic interactions of hydrogen and covalent bonding in this artificial nacre resulted in extraordinary mechanical properties, with tensile strength and toughness 4 and 10 times higher, respectively, than that of natural nacre. This integrated artificial nacre is promising for applications in many fields, such as aerospace, artificial muscles, tissue engineering, and especially flexible supercapacitor electrodes due to its high electrical conductivity. The use of synergistic interactions for toughening artificial nacres can serve as the basis of an alternative strategy for the construction of integrated, high-performance, GO-based nanocomposites in the future.

METHODOLOGIES

Materials. Graphene oxide was prepared by a modified Hummer’s method. Chitosan (medium molecular weight, 75–85% deacetylated) and 57 wt % HI were purchased from Sigma-Aldrich.

Preparation of GO-CS Hybrid Building Blocks. The CS was dispersed in 2% acetic acid solution with a concentration of 10 mg/mL and stirred for 24 h. The GO was dispersed in deionized water with a concentration of 0.5 mg/mL and stirred for 2 h, followed by CS solution addition with different GO/CS ratios under continuous
stirring. Subsequently, a suspension of GO-CS hybrid building blocks was sonicated for 30 min, and some alkali was added to stabilize these suspensions.

Preparation of GO-CS Nanocomposites. Vacuum filtration was applied to separate the homogeneous suspension of GO-CS hybrid building blocks into GO-CS nanocomposites. Then, GO-CS nanocomposites were chemically reduced by hydriodic acid for 6 h, and rGO-CS nanocomposites were obtained.

Characterization. Mechanical properties were conducted via a Shimadzu AGS-X Tester with a loading rate of 1 mm/min under a 20 N load cell. All measurements were conducted at room temperature, and all specimens were dried for 24 h at 45 °C before testing. The samples were cut into strips with a width of 3 mm and length of 10 mm, and the thickness of all samples was calculated by scanning electron microscopy (SEM). The Young’s modulus of all samples was determined by the slope of the linear region of the stress-strain curves. The toughness was calculated by the area under the stress-strain curve. The mechanical properties for each sample are based on the average value of 3–5 specimens. SEM images were recorded by a Hitachi S-4800 at 1–1.5 kV after sputtering a thin Pt/Au coating onto the samples. AFM was conducted by a Leica TCS SP5. The well-dispersed GO-CS solution was diluted with 100 times pure deionized water. Then, the diluted GO-CS dispersion was dropped on freshly cleaved mica and dried at room temperature to obtain the samples for the AFM measurement. The pure GO nanosheet sample for AFM testing was prepared in the same manner. TGA was performed on a TGA/DTA6300, NSK with a temperature increase rate of 10 K/min under nitrogen from 30 to 800 °C. The calculation of GO weight fraction in GO-CS nanocomposites is shown in the Supporting Information. Raman spectroscopy measurements were taken using a LabRAM HR800 (Horiba Jobin Yvon) with an excitation of 1.96 eV (633 nm). XPS measurements were carried out in an ESCALab220i-XL (ThermoScientific) using a monochromatic Al Ka X-ray source. X-ray diffraction profiles were taken with Cu Kα radiation (λ = 1.54 nm). The measurement was conducted with a voltage of 40.0 kV, a current of 30.0 mA, and a scanning speed of 4.0 degrees per minute. The electrical conductivities were tested by a standard two-probe method using a source meter (Agilent E4980A). The samples were cut into strips with a width of 3 mm and a length of 3–4 cm. Then, the two sides were fixed by silver paste for better contact with the probe. FTIR was obtained by a Thermo Nicolet Nexus-470 FTIR instrument with the attenuated total reflection mode (ATR). Each specimen was tested at three different points.

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

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Additional figures and tables (PDF)