Gelatin-assisted fabrication of graphene-based nacre with high strength, toughness, and electrical conductivity

Min Lian a,1, Jinchen Fan b,1, Zixing Shi a,*, Sai Zhang a, Hong Li a, Jie Yin a

a School of Chemistry and Chemical Engineering, State Key Laboratory for Metal Matrix Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China
b College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, People’s Republic of China

ARTICLE INFO

Article history:
Received 25 November 2014
Accepted 18 March 2015
Available online 25 March 2015

ABSTRACT

In this study, a high-performance graphene-based nacre was prepared using gelatin as a bioadhesive with the aid of the bending cycle-induced “mechanical annealed” effect. By this method, this type of graphene-based nacre is endowed with high strength, toughness, and electrical conductive properties, which is very different from other study where only one or two of three properties were improved. The maximum ultimate tensile strength can reach as high as 630.4 MPa when the optimal amount of gelatin was 30 wt%. Meanwhile, it has a high electrical conductivity of 42,624 S/m. Most notably, the periodic bending-induced “mechanical annealing” could further increase the ultimate tensile strength tremendously. After 100 cycles of periodic bending, the ultimate strength reached 902.1 MPa, with a high electrical conductivity of 44,780 S/m.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

As a novel material, graphene has elicited great interest for novel applications in energy storage technology [1,2], composites [3–5], mechanical actuators [6,7], optoelectronic devices [8,9], etc. Among these applications, nacres based on graphene and graphene oxide (GO) [10] have recently ignited significant interest in the scientific community owing to its great potential application for flexible sensors and biosensors [11,12], supercapacitors [13], electrocatalysts [14], drug delivery [15], etc. Many research groups have fabricated graphene-based nacres by flow-directed filtration of aqueous GO sheet dispersion [16,17] or solvent evaporation [18]. However, their mechanical properties on the macroscale are still orders of magnitude lower than individual GO at the nanoscale (strength: 63 GPa, modulus: 200–500 GPa) [19,20]. The main reason for this phenomenon is the lack of strong interaction among the graphene sheets under the tensile-stress mode. Accordingly, GO-based nacres will first be broken at interlayer contacts among the graphene sheets rather than the graphene sheet itself. Therefore, by mimicking the naturally occurring brick-and-mortar (B&M) structure from nacres, several research works were focused on strengthening the interaction of the adjacent graphene sheets (as brick) by the formation of cross-linking linkage among the interlayers of graphene in the presence of different types of adhesives, binders, or cross-linkers (as mortar). For example, Cheng et al. successfully prepared ultra-tough nacre-like GO papers...
by conjugating cross-linking GO sheets with π-conjugated 10,12-pentacosadiyn-1-ol [21]. Feng’s group also realized an ultrahigh modulus and high strength of GO papers through cross-linking between polydopamine-capped GO sheets and polyetherimide [22]. Nguyen et al. also prepared borate-cross-linking GO films with improved mechanical properties [23]. Although their mechanical properties were improved greatly, the films usually had low electrical conductive properties due to the presence of an insulated cross-linking agent and a broken conjugated structure after oxidation. Therefore, most of the research groups concentrated on the mechanical properties, rarely reporting the data related with the electrical properties. In order to improve the electrical properties for the graphene-based nacre, the conjugated sp² structure of the hydrophilic GO-based nacre was usually restored by chemical reduction [24]. However, the interaction between the adjacent graphene sheets was usually impaired by the removal of oxygen functional groups during the course of the reduced reaction, which would finally be harmful to the mechanical properties, especially toughness. Consequently, we faced a challenging situation for graphene-based nanocomposites wherein the parameters for improving the mechanical properties are detrimental to the electrical properties and the factors for increasing the electrical properties are unfavorable for improving the mechanical properties. Therefore, it is still highly challenging to prepare a graphene-based nacre with high strength, flexibility, and electrical properties simultaneously, all of which are essential factors in realizing their great potential application.

In this paper, we successfully proposed a solution for this challenge from three aspects. First, ultra-large graphene oxide (UGO) sheets with extremely high aspect ratios [25] were employed instead of conventional small graphene oxide (SGO) sheets to reduce the contact area of the individual sheets, which are conducive to enhancing the electrical and mechanical properties [26]. Second, gelatin was chosen as a bio-cross-linking agent toward GO sheets due to the function of gelatin in the leather industry and tissue engineering [27,28]. Furthermore, inspired by the self-reinforcing behavior well known for aligned polymer chains and other fibrous materials [29], we applied repeated bending cycle-induced mechanical annealing to better align the graphene nanosheet for further improving the mechanical properties of graphene-based nacre.

Gelatin is a linear polypeptide that consists of different amounts of 18 amino acids with distinctive advantages, such as nontoxicity, biodegradability and biocompatibility, cheapness, and commercial availability [30], and it has widely been used in the production of leather with high flexibility and mechanical properties due to its high chemical and physical interaction toward other components [31–33]. Owing to its weak negative character as a polyelectrolyte, gelatin is also widely used as a matrix in tissue engineering where electrical conductivity is required [28,30]. Considering the abundant amine pendant groups from gelatin and oxygen functional groups (such as epoxy) from GO sheets, gelatin can act as a cross-linking agent toward GO sheets via the ring-opening reaction between its amine groups and epoxy groups of GO sheets [34,35]. In fact, the gelatin-functionalized GO finds applications in cellular imaging and drug delivery, and we also found that gelatin can help exfoliate natural graphite in an aqueous solution due to its strong interaction toward graphene [36,37]. In fact, it is very difficult to find a chemical agent similar to gelatin that did show strong interaction toward both GO and graphene, which is beneficial in strengthening the interlayer action; even GO was reduced to graphene, which facilitates an increase in its electrical properties due to its negative polyelectrolyte.

Given the abovementioned facts, we prepared a graphene-based nacre using gelatin as a bioadhesive to cross-link UGO sheets by flow-directed filtration. After chemical reduction and the periodic bending-induced “mechanical annealing,” the final graphene-based nacre achieved a new record in electrical conductivity (44,780 S/m), the ultimate strength (902.1 MPa), and toughness (17.83 MJ/m²) for polymer-cross-linked graphene-based nanocoms, which are 8.5, 2.5, and 4.5 times higher than the highest reported data of the electrical conductivity [38], the ultimate strength [39], and toughness [40], respectively. Due to the combination of the exceptional mechanical strength and high electrical conductivity, our graphene-based nacre will certainly find many important potential applications in science and technology.

2. Experimental

2.1. Materials

Graphite powder (32 mesh, ~500 μm) was provided by Qingdao Jinrilai Graphite Co., Ltd. Sulfuric acid (H₂SO₄, 98%), nitric acid (HNO₃), phosphorus pentoxide (P₂O₅), potassium persulfate (K₂S₂O₇), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30%), gelatin, and hydroiodic acid (HI, 40%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (SCRC), and they were used as received.

2.2. Preparation of UGO dispersion

UGO was synthesized from graphite flakes by a modified Hummers method reported previously. In a typical procedure, graphite powder (6 g) was first treated with a mixture of H₂SO₄ (180 mL) and HNO₃ (60 mL) at room temperature (25 °C) for 24 h resulting in graphite intercalated compounds (GICs). Subsequently, expanded graphite (EG) was obtained by thermally expanding the dry GIC powder at 1000 °C for 10 s. Then EG (5 g) was pre-oxidized by vigorous stirring at 80 °C for 5 h in a mixture containing H₂SO₄ (300 mL), K₂S₂O₇ (4.2 g), and P₂O₅ (6.2 g). The pre-oxidized powder was kept at 35 °C and stirred for 4 h in a mixture of H₂SO₄ (550 mL) and KMnO₄ (25 g) to yield graphite oxide. This product was successively purified by seven cycles of wash with hydrochloric acid and deionized water to remove residual metal cations and acids, respectively. Finally, the colloidal dispersion of UGO sheets was achieved by vigorously stirring graphite oxide (30 mg) in 40 mL of deionized water for 12 h.
2.3 Fabrication of gelatin/ultra-large graphene oxide nacres and reduced gelatin/ultra-large graphene oxide nacres

Gelatin/ultra-large graphene oxide nacres (GUNs) were prepared using the method of flow-directed filtration of a homogeneous colloidal suspension of gelatin/large-GO with vacuum-assisted self-assembly. In brief, a certain volume of gelatin solution was added to the previously prepared UGO dispersion and vigorously stirred for 48 h in order to obtain a homogeneous dispersion of gelatin/UGO. The free-standing GUNs were prepared from the resulting uniform suspension by vacuum-assisted filtration through a cellulose membrane (47 mm in diameter, 0.22-μm pore size) followed by air drying and peeling off from the filter. The content of gelatin in GUNs varied from 0 to 35 wt%. For chemically reduced gelatin/ultra-large graphene oxide nacres (rGUNs), GUNs were directly immersed in an HI solution at 80 °C for 2 h and subsequently washed with 5 wt% bicarbonate solution and deionized water to completely remove the remnants of HI acid. Finally, the rGUNs were dried under vacuum at 60 °C for 12 h between two glass plates. The gelatin/small graphene oxide nacres (GSNs) and reduced gelatin/small-graphene oxide nacres (rGSNs) were synthesized using the same method.

2.4 Structure and property characterization

Fourier transform infrared (FTIR) spectroscopy was conducted on a Perkin-Elmer Paragon 1000PC spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted at room temperature using a Kratos Axis Ultra spectrometer (AXIS-UltraDLD, Kratos Analytical Ltd., Kyoto, Japan), equipped with a monochromatic Al Kα X-ray source with a power of 150 W. The C1s peak at 284.8 eV was used to calibrate the binding energy scale. X-ray diffraction (XRD) patterns were recorded on a BRUKER D8 ADVANCE using CuKα radiation (λ = 1.5418 Å). The dynamic mechanical tests were carried out on a dynamic mechanical analyzer (DMA) (DMA800, PerkinElmer, Waltham, MA, USA) with the temperature ranging from 25 to 500 °C; the frequency used was 1.0 Hz and the heating rate 5 °C/min. The Raman spectra were recorded using a Bruker Optics Senterra R200-L dispersive Raman microscope at an excitation wavelength of 532 nm. The mechanical properties of the composite nacres were measured with an Instron 4465 instrument at room temperature with a humidity of about 25% at a crosshead speed of 4 mm/min, and their initial gauge lengths were 10 mm. All samples were cut into rectangular strips of 4-mm width with a razor blade, and five strips were measured for each sample. The tensile fracture surfaces of the nacres were characterized by scanning electron microscopy (SEM) (Nova NanoSEM 450). The electric conductivity of the composite nacres was determined using a four-probe method (SB100A/21A, SH-METER) under a sample platform (SB120/2, SH-METER) equipped with parallel probes (probe spacing: 1 mm).

3 Results and discussion

The procedure for the preparation of the gelatin/UGO composite nacre involves four stages. In the first stage, UGO sheets were first exfoliated in water, and then gelatin solution was added into the aqueous suspension of UGO (Fig. 1a); immediate agglomeration was observed due to the strong interaction between the UGO sheets and the gelatin (Fig. 1b, left) [41]. After vigorous stirring, the agglomeration could be dispersed homogeneously again. In the second stage, the mixed solution was subjected to vacuum-assisted self-assembly to prepare the gelatin/UGO nacre. During this stage, the UGO sheets were cross-linked by gelatin. In the third stage, the obtained nacre was chemically reduced in the presence of HI to restore its electrical properties and increase its strength (Fig. 1b, right). The magnified and detailed schematic drawing of the composite nacre is shown in Fig. 1c. Meanwhile, the macroscopic appearance and the microscopic structure of the composite nacre are shown in Fig. 1d and e, respectively. Finally, the repeated bending cycles were applied to our nacre to induce “mechanical annealing” for better alignment of the reduced UGO (rUGO) sheets in the nacre with the intention of further improving its mechanical properties.

In order to demonstrate the key role that UGO sheets play in creating high-performance composite nacres, the corresponding GSNs were also prepared using the same procedure. The atomic force microscopy (AFM) image in Fig. 2a shows that the thickness of UGO sheets was measured to be ~1.0 nm, indicating the monolayered attribute of dispersed UGO sheets in water. Additionally, both AFM and SEM (Fig. 2b) observations suggest that UGO sheets are of relatively large size with lateral dimension over 50 μm. The area of UGO sheets ranged from about 50-5000 μm², while the areas of the SOG sheets were several square micrometers on average (Fig. S1 in Supplementary information (SI)). Such an enormous size of UGO sheets does play a vital role in preparing our high-performance graphene-based composite nacres (see below), given the unique nature of UGO sheets. Hereafter, the gelatin/UGO and gelatin/SGO nacres were severally abbreviated GUNx and GSNx, where x stands for the percentage composition of gelatin in nacres.

3.1 Characterization of interaction between gelatin and UGO

FTIR spectroscopy was first used to characterize the chemical interaction occurring during the formation of gelatin/UGO nacres. As illustrated in the spectrum of UGO (UGON) (Fig. 3a), several types of oxygen functionalities can be readily identified, namely, carboxyl (COOH, 1727 cm⁻¹), carbonyl (C=O, 1624 cm⁻¹), epoxy (C–O–C, 1226 cm⁻¹), and alkoxy (C–O, 1041 cm⁻¹) [42]. As for gelatin, the prominent broad peak around ~3500 cm⁻¹ is attributed to the stretching vibration of N–H coupling with the hydroxyl groups. The peaks at 1646 and 1535 cm⁻¹ are assigned to stretching vibration of the C=O and the stretching of C–N, respectively. After the UGO sheets are incorporated with gelatin (GUN30), the relative intensity of C–O–C at 1226 cm⁻¹ decreases, accompanied by the appearance of a new peak at 1535 cm⁻¹ corresponding to the stretching of C–N bonds, which indicates that an epoxide ring-opening reaction via the nucleophilic attack of amine groups has taken place between UGO and gelatin [34,41]. Meanwhile, the carboxyl
peak at 1724 cm$^{-1}$ is significantly weakened, which is associated with hydrogen bonding between amines (or ammonium ions) of gelatin and hydroxyl groups on the basal plane of GO along with ionic binding of ammonium ions to deprotonated hydroxyl groups [35,43].

XPS also provided additional support for the reaction chemistry between gelatin and UGO sheets. The XPS spectrum of gelatin (Fig. S2a in SI) shows three component elements, C, N, and O, and its high-resolution C1s XPS spectrum (Fig. S2b in SI) can be fitted into four peaks with
the binding energy at 284.7, 285.6, 286.3, and 288.0 eV, corresponding to the C=C/C–C, C–OH, C–N, and C=O groups, respectively. While the C/O atom ratio of UGON is 3.07, it shifts to 3.82 for the GUN30 due to the partial reduction by gelatin [36,44]. Meanwhile, a new component of N of about 1.86% is observed by the introduction of gelatin. After treatment with HI, the C/O atom ratios of rUGON and rGUN30 are significantly increased to 8.54 and 6.98, respectively, due to the efficient elimination of oxygen functionalities. The deconvoluted C1s XPS spectrum for UGON (Fig. 3b) has five discernible signals, namely, C=C/C–C (284.7 eV), C–OH (285.6 eV), C–O–C (286.9 eV), C=O (288.2 eV), and C (O)–
O (289.4 eV) in line with the report in the literature [45]. By contrast, the C1s spectrum for GUN30 (Fig. 3c) shows significantly decreased and increased components for C–O(C and C–OH, respectively. In the meantime, a new component assigned to C–N bond (286.5 eV) is also observed, which is a strong support for the ring-opening reaction between amine groups in gelatin and epoxides in UGO sheets [35]. After chemical reduction by HI, the peak intensity of oxygen-containing functionalities of rUGON and rGUN30 (Figs. 5c in SI and 3d) is substantially decreased except for the slight signal strengthening for C–OH. Notably enough, the signal for the C–N bond in rGUN30 is significantly increased compared to that of GUN30, most likely attributed to the additional ring-opening reaction during the HI reduction procedure, which is also reflected in the results of the remarkably increased mechanical properties for GUNs after HI reduction (Fig. 5c).

The structure changes during the fabrication of the nacre were further monitored by XRD, as shown in Fig. 4a. While the UGOP shows a sharp peak at 2θ = 10.86° with a d-spacing of 8.15 ± 0.04 Å, there is a well-defined dominant peak located at 10.24° corresponding to an interlayer distance of 8.64 ± 0.07 Å in the XRD pattern of GUN30. The increased d-spacing indicates that the molecular chains of gelatin were successfully embedded into the UGO sheets through covalent and non-covalent interation between gelatin and UGO sheets. The well-defined dominant peak (GUN30) suggests that a well-ordered structure was formed for the graphene-based nacre by the incorporation of gelatin. At the same time, a weaker peak at 22.34° was observed, which indicates that the UGO sheets were partially reduced by gelatin [36,44]. After reduction, the interlayer spacing of the rGUN30 was decreased to 3.73 ± 0.02 Å (2θ = 23.82°), higher than 3.70 ± 0.02 Å (2θ = 24.02°) of the rUGON, indicating that the gelatin was still immobilized between rUGO sheets due to the strong covalent and non-covalent interaction between graphene and gelatin. In addition, the rGUN30 has a smaller interlayer spacing (3.73 ± 0.02 Å) than rGSN25 (3.76 ± 0.01 Å), and this reduced spacing could suggest that nacres based on ultra-large graphene (GUNs) have more compact and closer-stacked layered structures than small graphene-based nacres (GSNs), which could be beneficial in improving the mechanical and electrical properties.

The change in the structural defects for the UGO-based nacre was also explored using Raman spectroscopy, as depicted in Fig. 4b. It is clear that the intensity ratios of the D band to G band, namely, the $I_D/I_G$ ratio, increases from 0.972 ± 0.03 for the UGN to 0.979 ± 0.02 for the GUN30. The increased $I_D/I_G$ ratio of GUN30 is the consequence of the formation of a C–N bond on the graphene basal plane modified by gelatin [39], which is a strong support for the reaction between amine groups of gelatin and epoxides of UGO. Analogously, after HI reduction, the $I_D/I_G$ ratio of rUGON and rGUN30 is increased to 1.390 ± 0.06 and 1.344 ± 0.04, respectively, indicating that the reduction process altered the structure of rUGO sheets with a high quantity of structural defects [46]. Meanwhile, the $I_D/I_G$ ratio of rGUN30 is less than that of rUGON, which reveals that relatively lower structural defects of rGUN30 were generated during the reduction process. Besides, the newly presented 2D bands (~2672 cm$^{-1}$) for the reduced nacres (rUGON, rGUN30, and rGSN25) confirm that the crystal defects are substantially reduced with graphitization successfully achieved in the reduced nacres [47]. Compared to rGSN25, rGUN30 has a lower value of $I_D/I_G$ ratio, which indicated fewer defects in the ultra-large graphene system. The additional thermogravimetric analysis (TGA) is displayed in Fig. S3 in SI. It is obvious that the addition of gelatin can greatly improve the thermal stability of the oxygen-containing groups of GUN30, owing to the covalent bonding of gelatin to UGO sheets.

### 3.2. Mechanical properties after different stages

The analysis results for FTIR, XPS, XRD, and Raman spectroscopy show that there are strong chemical and physical interactions between the graphene and gelatin, which also reflect the final mechanical properties of graphene-based nacre. Fig. 5a shows the representative stress–strain curves of the graphene-based nacres intercalated with the gelatin at different stages. As shown in Fig. 5b, the presence of gelatin obviously increases the mechanical properties of the

---

![Fig. 4 – (a) XRD patterns of gelatin and different types of nacres. (b) Raman spectra of these nacres. (A color version of this figure can be viewed online.)](image-url)
graphene-based nanocomposites. For example, 10 wt% of gelatin could increase the tensile strength from 57.9 ± 4.5 MPa for the pure UGO nacre (UGON) to 122.7 ± 7.5 MPa with increases of 111.9%. Further increasing the concentration of gelatin up to 30 wt%, the maximum data on the ultimate tensile strength and Young’s modulus were obtained at 261.9 ± 15.8 MPa and 27.84 ± 2.24 GPa (GUN30). After HI reduction, the ultimate tensile strengths of reduced graphene-based nanocomposites were significantly improved (Fig. 5c). For example, the ultimate tensile strength of rGUN30 reached 630.4 ± 30.5 MPa, increasing by 452%, as compared with the sample before reduction. Most importantly, the elongations at break of reduced graphene-based nanocomposites did not decrease but they were augmented after reduction. For example, as shown in Fig. 5a, compared with that of rUGON, the elongation at break of the rGUN30 is 2.54%, corresponding to the toughness of ∼8.88 MJ/m^3, and these data indicate that the introduction of gelatin maintains the flexibility of graphene-based nanocomposites, which is very different from the results obtained from other studies wherein the toughness is usually compromised by an increase in the strength and modulus [22,23]. The relevant nacre-like SEM images for the graphene-based nanocomposites are illustrated in Fig. S4 in SI.

This high toughness could cause the sample (rGUN30) to withstand the repeated bending cycle-induced “mechanical annealing” without being broken. By this method, the mechanical properties are expected to further improve. The details for one cycle of the bending process are illustrated in Fig. 5d. Surprisingly, the mechanical properties of rGUN30 were found to improve tremendously after repeated bending cycles. The typical stress–strain curves for rGUN30 after various bending cycles are displayed in Fig. 5e and f. After 100 bending cycles, the maximum ultimate strength and toughness of rGUN30 are 902.1 ± 90.4 MPa and ∼17.83 MJ/m^3, increasing by 43.1% and 100.8%, respectively, as compared with those of pristine rGUN30. DMA was further applied to investigate the bending-induced enhancement effect on the storage modulus. As shown in Fig. S5 in SI, the storage modulus for rGUN30 is increased with increase in bending cycles, and after the sample was subjected to 100 bending cycles, its storage modulus was found to be ∼27.09 GPa (room temperature), which is almost increased by 6.86 GPa in contrast to that of pristine rGUN30 (~20.23 GPa). On analyzing the mechanical properties of graphene-based nacre after different bending cycles, the strength, modulus, and toughness of the nacre were found to increase simultaneously, and the strength and toughness are the highest values as compared with the several representative published results (see Table S2 in SI). Based on the literature, it is found that increasing the strength and modulus is usually accompanied by the low toughness. For example, Nguyen reported the highest stiffness (modulus) of 127 GPa for borate-cross-linked graphene nacre (B–GO) [23]. However, only 0.15% of strain and 0.14 MJ/m^3 of toughness are observed for B–GO, which indicates that this type of nacre is easily broken due to its high brittleness (low toughness). Feng used polyetherimide to cross-link the dopamine-modified graphene to produce a nacre with a tensile strength of 209.9 MPa and very low toughness. This high toughness could cause the sample (rGUN30) to withstand the repeated bending cycle-induced “mechanical annealing” without being broken. By this method, the mechanical properties are expected to further improve. The details for one cycle of the bending process are illustrated in Fig. 5d. Surprisingly, the mechanical properties of rGUN30 were found to improve tremendously after repeated bending cycles. The typical stress–strain curves for rGUN30 after various bending cycles are displayed in Fig. 5e and f. After 100 bending cycles, the maximum ultimate strength and toughness of rGUN30 are 902.1 ± 90.4 MPa and 17.83 MJ/m^3, increasing by 43.1% and 100.8%, respectively, as compared with those of pristine rGUN30. DMA was further applied to investigate the bending-induced enhancement effect on the storage modulus. As shown in Fig. S5 in SI, the storage modulus for rGUN30 is increased with increase in bending cycles, and after the sample was subjected to 100 bending cycles, its storage modulus was found to be 27.09 GPa (room temperature), which is almost increased by 6.86 GPa in contrast to that of pristine rGUN30 (~20.23 GPa). On analyzing the mechanical properties of graphene-based nacre after different bending cycles, the strength, modulus, and toughness of the nacre were found to increase simultaneously, and the strength and toughness are the highest values as compared with the several representative published results (see Table S2 in SI). Based on the literature, it is found that increasing the strength and modulus is usually accompanied by the low toughness. For example, Nguyen reported the highest stiffness (modulus) of 127 GPa for borate-cross-linked graphene nacre (B–GO) [23]. However, only 0.15% of strain and 0.14 MJ/m^3 of toughness are observed for B–GO, which indicates that this type of nacre is easily broken due to its high brittleness (low toughness). Feng used polyetherimide to cross-link the dopamine-modified graphene to produce a nacre with a tensile strength of 209.9 MPa and very low toughness. This high toughness could cause the sample (rGUN30) to withstand the repeated bending cycle-induced “mechanical annealing” without being broken. By this method, the mechanical properties are expected to further improve. The details for one cycle of the bending process are illustrated in Fig. 5d. Surprisingly, the mechanical properties of rGUN30 were found to improve tremendously after repeated bending cycles. The typical stress–strain curves for rGUN30 after various bending cycles are displayed in Fig. 5e and f. After 100 bending cycles, the maximum ultimate strength and toughness of rGUN30 are 902.1 ± 90.4 MPa and 17.83 MJ/m^3, increasing by 43.1% and 100.8%, respectively, as compared with those of pristine rGUN30. DMA was further applied to investigate the bending-induced enhancement effect on the storage modulus. As shown in Fig. S5 in SI, the storage modulus for rGUN30 is increased with increase in bending cycles, and after the sample was subjected to 100 bending cycles, its storage modulus was found to be 27.09 GPa (room temperature), which is almost increased by 6.86 GPa in contrast to that of pristine rGUN30 (~20.23 GPa). On analyzing the mechanical properties of graphene-based nacre after different bending cycles, the strength, modulus, and toughness of the nacre were found to increase simultaneously, and the strength and toughness are the highest values as compared with the several representative published results (see Table S2 in SI). Based on the literature, it is found that increasing the strength and modulus is usually accompanied by the low toughness. For example, Nguyen reported the highest stiffness (modulus) of 127 GPa for borate-cross-linked graphene nacre (B–GO) [23]. However, only 0.15% of strain and 0.14 MJ/m^3 of toughness are observed for B–GO, which indicates that this type of nacre is easily broken due to its high brittleness (low toughness).
toughness (0.23 MJ/m$^3$) [22]. Cheng reported the strong integrated strength and toughness graphene-based nacre (PDA–RGO), where the tensile strength reaches up to 204.9 MPa and the toughness is about 4 MJ/m$^3$ [40]. Tsukruk produced silk–graphene nacre (SL–RGO) with a tensile strength of 300 MPa and a toughness of 3.4 MJ/m$^3$ [48,49]. As compared with those representative published data, the tensile strength and toughness of rGUN30 with 100 bending cycles are still 2.5 and 4.5 times higher than the highest reported data [39,40].

3.3. Electrical properties

After chemical reduction with HI, there is a tremendous rising trend of electrical conductivities for graphene-based nacres due to the elimination of oxygen-containing groups and effective recovery of sp$^2$-hybridized chemical structure in rUGO sheets. As seen from the visual photos of the rGUN30 (Fig. 1d), the sample exhibits metallic luster, which suggests the effective chemical reduction of graphene-based nacres by HI. By the four-point probe test method (Fig. 6a), the electrical conductivity shifts to around ~40,000 S/m for graphene-based nacres with selected contents of gelatin and electrical conductivity of rGUN30 reaches up to ~42,624 S/m. As shown in Fig. 6e and f, the rGUN30 is directly used as a length of wire for lightening the LED (light-emitting diode) light in a test circuit due to its high electrical conductivity. After 100 bending cycles (Fig. 6b), the electrical conductivity of rGUN30 was further increased to ~44,780 S/m, which is 8.5 times higher than the highest reported conductive data (5265 S/m) for polymer-cross-linked graphene composite nacres reported by Liao [38].

3.4. Discussion

From the analysis of mechanical and electrical properties, it is found that gelatin-cross-linked graphene nacres show a remarkable combination of strength, toughness, and electrical properties. Several important factors may explain these remarkable results. First, gelatin is natural macromolecular protein material consisting of a large amount of amino groups and carboxylic acid groups [36]. Strong hydrogen bonding exists between the amino groups from gelatin and the carboxyl groups from UGO. In the meantime, FTIR and XPS have demonstrated that amino groups from gelatin could also react with epoxy groups from the surface of UGO sheets to form the cross-linking linkage. It is also found that gelatin solution can effectively help exfoliate graphite and carbon nanotubes in water due to its amphiphilic nature [37]. Therefore, gelatin can act as a high-efficiency adhesive to graphene due to its strong interaction toward GO and graphene in both chemical and physical modes. These synergistic effects of non-covalent and covalent interactions contributed to the enhancement of the tensile strength of graphene-based nacre. At the same time, the long chain of the high molecular weight of gelatin can also provide the graphene more free space for movement under the stress, which gives the graphene–nacre its high toughness just as gelatin offers cross-linked leather more toughness [21]. In addition, as a weak net negative charge polyelectrolyte, gelatin can also help improve the electrical conductivity toward reduced graphene [28,30]. Second, UGO has several significant advantages such as extremely high aspect ratios [25,26] and excellent mechanical properties, as well as contributing to lower inter-sheet contact resistance [50–53], which facilitate an increase in the mechanical and electrical properties of the UGO-based nacre. In this paper, the corresponding GSNs were also prepared for comparison. As a result, the highest mechanical

---

Fig. 6 – (a) Electrical conductivities of nacres as a function of gelatin content. Inset: schematic diagram of four-point probe measurement. (b) Electrical conductivities for rGUN30 after different bending cycles. (c–f) Digital photos for the conductivity measurements of rGUN30: the test circuit is (c) disconnected and (d) connected; (e) semicircular sample (diameter: 47 mm) and (f) rectangular sample (size: 40 x 4 mm) are tested in the circuit. (A color version of this figure can be viewed online.)

Fig. 7 – XRD patterns of rGUN30 after different bending cycles. (A color version of this figure can be viewed online.)
properties of rGSN25 were found to be 420.5 ± 22.9 MPa for the tensile strength, 18.79 ± 1.06 GPa for the modulus, ~4.79 MJ/m³ for toughness (Fig. 5c), and ~39,785 S/m (Fig. 6a) for the electrical conductivity, which are much lower than ultra-large graphene-based nacres. Such a comparison verifies the important role of UGO sheets in improving the mechanical properties of graphene-based nacres. Finally, the bending cycle-induced “mechanical annealing” could also further improve the mechanical properties of the graphene-based nacre. XRD was used to characterize the structure changes of the rGUN30 after different bending cycles. As shown in Fig. 7, the shape of the peaks becomes increasingly sharper and the peak intensity becomes increasingly stronger with the increase of bending cycles, and the 2θ value of the peak for rGUN30 gradually increased from 23.82° to 24.19° after 100 bending cycles. The results from XRD supported the possibility of periodic bending leading to even tighter packing of rUGO sheets and improving the long-range order for rGUN30. SEM images (Fig. 8a–e) were also used for characterizing the fracture surfaces for rGUN30 after various bending cycles. It can be clearly seen that the sheets are compactly stacked together after 100 bending cycles, which is in line with the results from XRD. Therefore, during the bending process, the rUGO sheets in rGUN30 would lead to a better alignment under the loading of bending stress. By this method, the individual rUGO sheets increase their interaction toward each other through chemical linkage with gelatin, which eventually resulted in an increase in the mechanical properties of ultra-large graphene-based nacres.

4. Conclusions

We use gelatin as an active bioadhesive to prepare graphene-based nacres. Compared with other graphene-based nacres, the nacres in our study possess several remarkable characteristics. First of all, gelatin showed compatibility toward both GO and graphene. Therefore, the interaction between graphene layers is strengthened by the presence of gelatin. Considering its low cost and abundance in nature, gelatin provides a strong basis for the fabrication of high-performance graphene-based nacres at an industrial scale. Next, the use of UGO sheets reduces the contact areas, which is conducive to increasing the strength and electrical properties of our UGO-based nacres. Finally, by the method of “mechanical annealing,” the alignment of rUGO sheets in the nacre could be further improved, and the final mechanical and electrical properties were also increased simultaneously. All these factors contribute to the production of UGO-based nacres with high strength, toughness, and electrical conductivity. Thus, our gelatin-cross-linked UGO-based nacre will surely be a promising material for many technological and engineering applications with immense potential as flexible electrodes to engineering materials in the near future.

Acknowledgments

We acknowledge the support from National Nature Science Foundation of China (No. 51473091). We are grateful to researchers in the instrument analysis center of the Shanghai Jiao Tong University for their help in material analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2015.03.045.

REFERENCES


