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

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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.

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

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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-linked 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 sp^2 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 nacres 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/m^3) for polymer-cross-linked graphene-based nacres, which are 8.5, 2.5, and 4.5 times higher than the highest reported data of the electrical conductivity (5265 S/m) [38], the ultimate strength (360 MPa) [39], and toughness (4.0 MJ/m^3) [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 (H_2SO_4, 98%), nitric acid (HNO_3), phosphorus pentoxide (P_2O_5), potassium persulfate ($K_2S_2O_8$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 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 H_2SO_4 (180 mL) and HNO_3 (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 H_2SO_4 (300 mL), $K_2S_2O_8$ (4.2 g), and P_2O_5 (6.2 g). The pre-oxidized powder was kept at 35 °C and stirred for 4 h in a mixture of H_2SO_4 (550 mL) and $KMnO_4$ (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.