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Bioinspired graphene-based nanocomposites *via* ionic interfacial interactions

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ABSTRACT

In nature, small amount of metal ions play a critical role in improving mechanical properties, such as the jaws of marine polychaete Nereis and Glycera. Recently, the multivalent cations metals have been successfully introduced to enhance the interfacial strength of graphene based-nanocomposites through forming ionic cross-linking networks with graphene oxide (GO) nanosheets by coordination. Combination with other interfacial interactions, the synergistic effect was constructed in the resultant bioinspired nanocomposites, leading to outstanding integrated performance, including thermal, electrical, fatigue resistant and mechanical properties. These excellent properties make this bioinspired graphene-based nanocomposites to be great candidates for applications in many fields, for example, flexible electronics devices, artificial muscles, supercapacitors, and aerospace.

1. Introduction

Biominerals are extensively exploited to tough or harden biological tissues with the abundant inorganic components in living organisms [1,2]. In 1980, Bryan and Gibbs first reported high concentrations of metals such as copper (13% w/w), manganese (~20% w/w) and zinc (~30% w/w) in the jaws of marine polychaete Nereis and Glycera [3,4]. Multivalent metal ions are intentionally infiltrated into the protein structures of biological tissues to form a metal-infiltrated protein matrix, which greatly improve their mechanical properties [1,3,5–7]. For instance, the nanoindentation strategy of testing the modulus and hardness of the Nereis jaws before and after Zn^{2+} chelation was designed and performed, revealing that the Zn^{2+} played a key role in reinforcing the stiffness and hardness of biomaterials [8]. Lee et al. [9] incorporated zinc, aluminum, or titanium into the inner protein structures of spider dragline silks by multiple pulsed vapor-phase infiltration (MPI). The metal-incorporated silks showed a great improvement in toughness, which serve as a potential approach for enhancing the mechanical properties of other biomaterials, and the schematic of a proposed metal infiltration mechanism into the silk protein was shown in Fig. 1a [9]. The egg shell membranes also showed much greater mechanical properties after infiltrated metal ions (Al^{3+}, Ti^{4+} and Zn^{2+}), and the stress-strain curves of metal infiltrated collagen membranes of an avian egg were listed in Fig. 1b [9]. In addition, DNA and RNA could been hydrolyzed by some metal ions under physiological conditions [10–13], the mechanisms of these remarkable catalysis were elucidated clearly by Komiyama [12]. Zhang et al. [14] first demonstrated that graphene oxide (GO) combining with copper ions was able to disconnect DNA, the DNA cleaving system of GO/Cu^{2+} could manipulate these DNA and RNA instead of naturally-occurring enzymes, which had many promising applications in biotechnology, and the proposed mechanism was shown in Fig. 1c. Therefore, it is an effective strategy to introduce metal elements to enhance the performance of the biological materials.

With the recent study of biomimetic materials, graphene oxide (GO), a water-soluble derivative of graphene with abundant surface functional groups, is one of the best promising building blocks for constructing bioinspired materials, such as 1D fibers, 2D films, three-dimensional (3D) monoliths and gels. The functional surface groups of GO nanosheets enable interface designs between GO nanosheets and other polymers/cross-linking agent to improve the interfacial strength, resulting in great enhancement in the load transfer efficiency and the mechanical properties of bioinspired nanocomposites. The interface designs for bioinspired materials are generally categorized into hydrogen bondings, ionic bondings, π–π interactions and covalent bondings, respectively. Hydrogen bondings are easily formed in graphene-based nanocomposites, for example, the bioinspired GO-polyvinyl alcohol (PVA) nanocomposites possessed high Young's modulus and tensile strength due to high density of hydrogen bonding networks between adjacent GO nanosheets and PVA chains, as well as between

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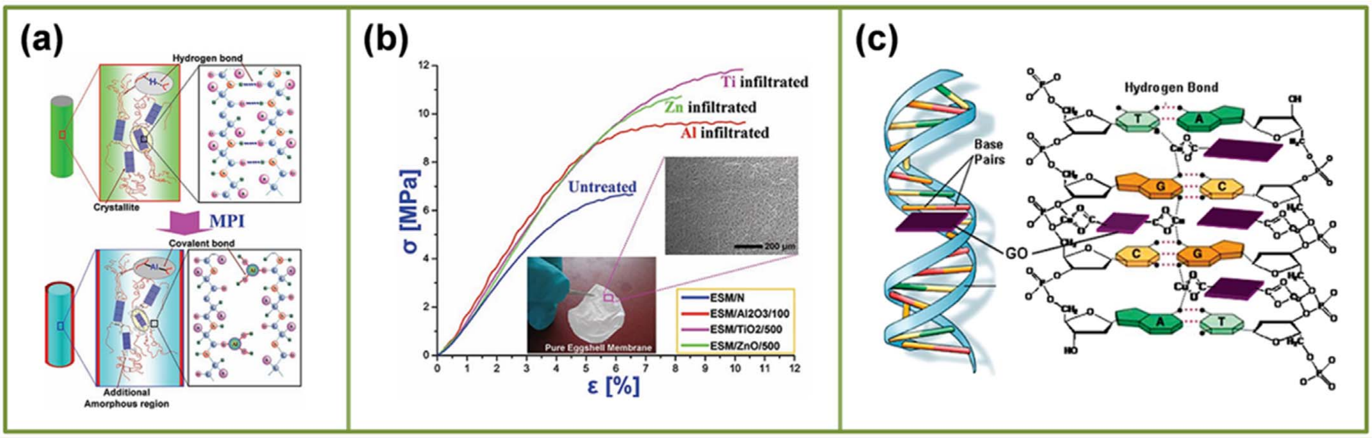

Fig. 1. (a) Schematic description of a proposed metal infiltration mechanism into the silk protein by the multiple pulsed vapor-phase infiltration process. Reproduced from Ref. [9] with permission from Copyright © 2009 The American Association for the Advancement of Science. (b) Stress-strain curves of different metals infiltrated collagen membrane of an avian egg. Reproduced from Ref. [9] with permission from Copyright © 2009 The American Association for the Advancement of Science. (c) Proposed DNA cleavage mechanism by the GO/Cu^{2+} system. Reproduced from Ref. [14] with permission from Copyright © 2010 American Chemical Society.

GO nanosheets and water molecules [15]. Ionic bondings exist in metal ions modified robust graphene-based nanocomposites, which have been assembled by coordination of multivalent metal ions with the functional groups of GO nanosheets [15]. The π–π interactions are formed between conjugated molecules with pyrene derivatives and GO nanosheets, which show a strong advantage of simultaneously improving electrical conductivity and interfacial strength [16]. Covalent bonding with high bond energies possesses powerful interfacial strength, which is adjusted by changing the crosslinking density and length of the molecular chain. Small molecule crosslinkers can improve the strength and stiffness but sacrifice the toughness, mainly due to the limitation of sliding between adjacent GO nanosheets [16]. In this review, the ionic interfacial interactions in graphene-based nanocomposites have been chosen and discussed in detail due to the specific role of inorganic components in biomimetic materials.

The bioinspired strategies for fabricating the graphene-based nanocomposites with ionic interfacial designs are shown in Fig. 2. In the early stage, the metal ions have been solely to construct the interfacial interactions [17], but the mechanical properties are not highly enhanced due to weak ionic-bonding. Then, the synergistic effect was formed through combining ionic bonding and other interfacial interactions, such as hydrogen bonding, π-π interaction, and covalent bonding. A series of high performance bioinspired graphene-based nanocomposites with the synergistic effect are demonstrated, including 1D fiber in Fig. 2e [18], 2D films in Fig. 2a [19], 2c and 2d [20], and 2f [21], and 3D aerogels in Fig. 2b [22].

2. Ionic interfacial interactions for graphene-based nanocomposites

Recently, some multivalent metal ions have been introduced into graphene-based nanocomposites for constructing the ionic interfacial

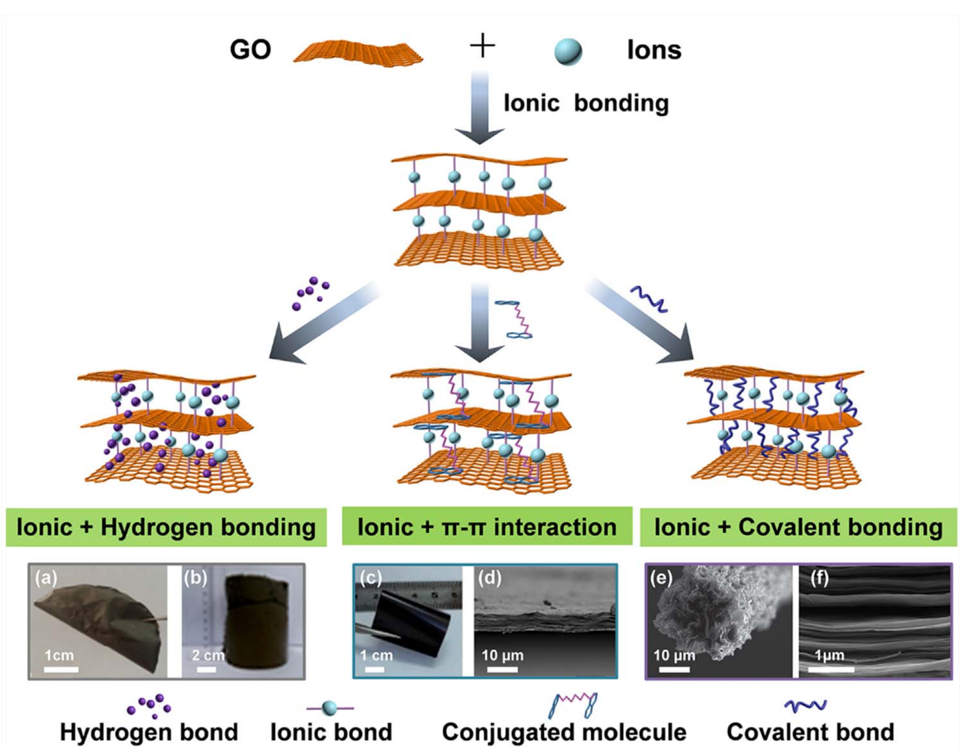

Fig. 2. Schematic diagram of the bioinspired strategy for fabricating the graphene-based nanocomposites with ionic interfacial interactions, the followings are the digital photographs or morphologies with different synergistic effects. (a) The digital photograph of 2D bioinspired graphene-based nanocomposites films (Reproduced from Ref. [19] with permission from Copyright © 2016 Springer) and (b) the digital photograph of 3D excellent compressible graphene-based aerogels (Reproduced from Ref. [22] with permission from Copyright © 2015 John Wiley and Sons) with the synergistic toughening effect of ionic bonding and hydrogen bonding; (c) The digital photograph and (d) cross-section morphology of flexible Eu^{3+}-crosslinked GO/PAAP nanocomposites with the synergy of ionic bonding and π-π interaction, as well as hydrogen bonding. Reproduced from Ref. [20] with permission from Copyright © 2016 John Wiley and Sons. (e) The digital photograph of 1D ultra-strong graphene-based fibers (Reproduced from Ref. [18] with permission from Copyright © 2016 John Wiley and Sons) and (f) cross-section morphology of robust 2D rGO-Zn^{2+}-PCDO films (Reproduced from Ref. [21] with permission from Copyright © 2016 Royal Society of Chemistry) with the synergistic interaction of ionic bonding and covalent bonding.