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Enhanced mechanical properties, water stability and repeatable shape recovery behavior of Ca^{2+} crosslinking graphene oxide-based nacre-mimicking hybrid film

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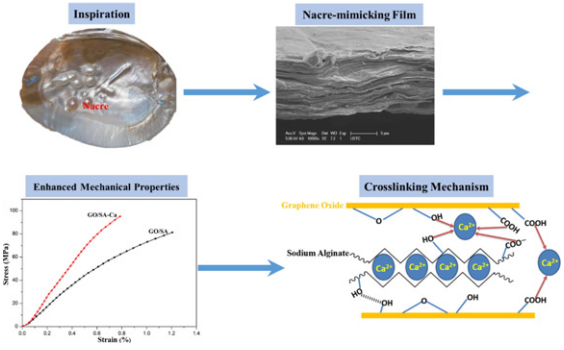
HIGHLIGHTS

- Nacre mimicking film was prepared using graphene oxide and sodium alginate as bricks and mortar, respectively.
- To further improve mechanical properties of artificial hybrid film, Ca^{2+} was employed as a green crosslinker.
- The hybrid film exhibited enhanced water stability and repeatable shape recovery behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

Artificial nacre-like inorganic-organic hybrid films are fabricated by a facile evaporation-induced self-assembly method using graphene oxide (GO) nanosheets as rigid bricks and a natural polysaccharide of sodium alginate (SA) as soft mortar. To further improve tensile mechanical properties of the GO/SA films, Ca^{2+} is utilized as a substitute for the most widely used glutaraldehyde to crosslink the films. Owing to the high chelation affinity for metal ions, the Ca^{2+} modified (Ca-GO/SA) films show higher tensile mechanical properties than those of the original samples. Water uptake in the Ca-GO/SA film is greatly decreased and water stability is improved by the introduction of Ca^{2+}. The Ca-GO/SA films exhibit water-triggered shape recovery behavior. The films show two-way shape memory effect and possess two original shapes, which can be reversibly transformed by immersion in water and removal of the absorbed moisture. This advanced hybrid film will broaden the applications for biomimetic materials and shows potential for applications in the fields of water-sensitive actuators and sensors.

1. Introduction

Graphene, a one-atom-thick two-dimensional (2D) carbon nanosheet, has captured enormous scientific attention in recent years, due to its extraordinary mechanical, thermal, electrical and optical properties [1]. The oxidized form of graphene, graphene oxide (GO), is widely used as a precursor to graphene preparation via chemical or thermal reduction processes [2]. GO is commonly prepared by oxidizing raw graphite according to the Hummers method [3]. Upon oxidization, various oxygen functional groups, such as hydroxyl and epoxide groups on the basal planes and carboxyl groups at the sheet edges, are produced

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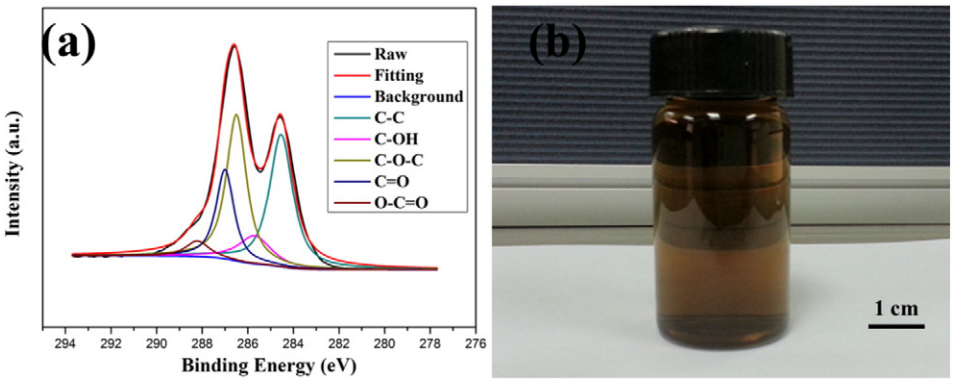

Fig. 1. (a) C1s XPS spectrum of GO; (b) Photograph of GO aqueous dispersion.

on the GO nanosheets [4]. These oxygen functionalities enable easy exfoliation of the GO into monolayer nanosheets in water under ultrasonication or stirring [2]. Wallace et al. have found that GO nanosheets in aqueous dispersion are highly negatively charged, due to the ionization of the carboxyl and hydroxyl groups [5]. Thus, GO nanosheets may be regarded as anionic polyelectrolytes and be expected to show strong interactions with metal ions. Some investigations have already been conducted into the binding properties of GO with metal ions, especially divalent cations [6–9]. Ruoff et al. have demonstrated that the alkaline earth metal ions (Mg^{2+} and Ca^{2+}) can significantly improve mechanical properties of GO papers via the coordination effects of these ions with the carboxylate groups on GO nanosheets [9]. Furthermore, divalent and trivalent metal ions can promote the self-assembly of GO nanosheets into hydrogels, via the interactions between these

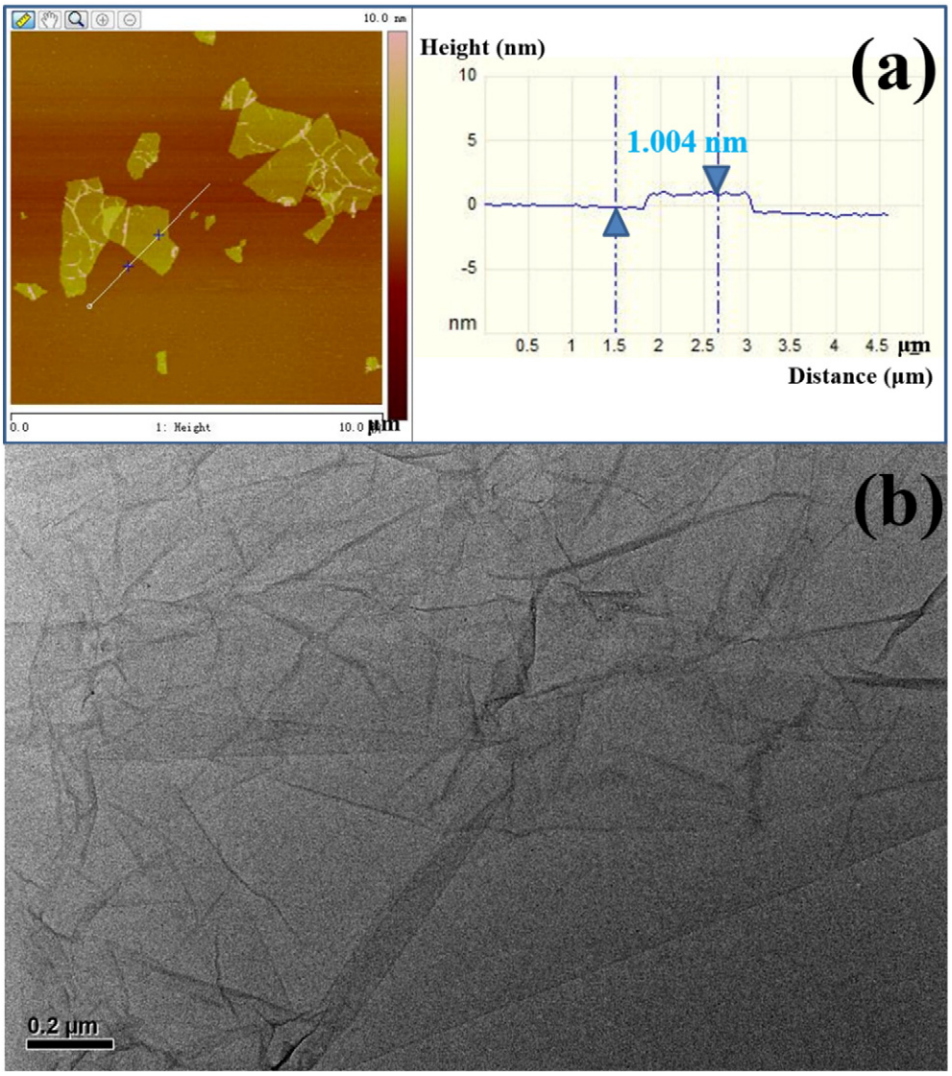

Fig. 2. (a) AFM image of GO nanosheets and the corresponding height profile along the white line; (b) TEM image of GO.