Full Length Article

Preparation and properties of three dimensional graphene/phenolic resin composites via in-situ polymerization in graphene hydrogels

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ABSTRACT

Three dimensional graphene/phenolic resin (3DGP) composites were synthesized via in-situ polymerization in graphene hydrogels (GHs). The water in the GH was perfectly replaced with resole resin due to the infiltration of resole resin into the GH and the evaporation of water from the GH by heating in the appropriate temperature. The 3DGP composite was obtained successfully by in-situ polymerization. The prepared composite can retain the complete 3D network structure to achieve good dispersion of graphene sheets forming 3D conducting network in polymer. The mechanical and electrical properties were measured, and the results showed that the composite possessed good electrical conductivity and compressive property. The compressive strength of 3DGP composite (441.11 MPa) increased by 14.24% compared with that of pure phenolic resin. In addition, the electrical conductivity of 3DGP composite reached 2.73 S/cm with a graphene loading of 2.15 wt% due to the 3D interconnected structure.

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1. Introduction

In recent years, graphene, a two-dimensional, one-atom-thick sheet of sp^2-hybridized carbon atoms, has received a lot of attention in a variety of fields like high-strength materials, electronic devices, energy storage, sensors and supercapacitors because of its excellent electrical, thermal and mechanical properties [1–4]. Incorporating graphene into other materials to prepare composites is an efficient way to utilize graphene. Graphene-related composites mainly have three types: graphene/metal composites, graphene/ceramic composites and graphene/polymer composites [5]. The graphene/polymer composites have been extensively studied for their outstanding performances. Conventional methods for integrating graphene sheets include melt-blending, solution-blending, and in-situ polymerization [4]. In the process of synthesizing graphene/polymer composites, it is difficult to achieve good dispersion of graphene sheets in polymer due to the strong π-π interaction between graphene sheets [6,7]. To overcome this problem, a lot of efforts have been dedicated to assemble graphene into three dimensional (3D) network materials such as hydrogels, aerogels and graphene foam (GF) [8–16]. Assembling individual graphene sheets into 3D structures can simultaneously achieve good dispersion of graphene sheets and 3D conducting network. The 3D network structure can realize the transmission of external force

in the graphene composites and prevent the microcracks from expanding to improve the mechanical strength of composites. At the same time, the 3D interconnected network can endow the composites with good electrical conductivity and thermal conductivity [8–10,17,18]. Compared to the material synthesized by conventional dispersion of graphene sheets, the graphene/polymer composites in which graphene sheets are assembled into 3D structures can exhibit significantly improved electrical, thermal and mechanical properties [19]. At present, there are a variety of methods for synthesizing 3D graphene including template-directing method, cross-linking method, directed chemical vapor deposition, and in-situ reduction-assembly method [20–22]. In general, using graphene oxide (GO) to synthesize 3D graphene is quite suitable due to its rich functional groups and good dispersability in aqueous media. GO could be reduced to graphene under hydrothermal treatment or in the presence of reducing agents. During the GO reduction reaction, GO could be self-assembled together to form a 3D architecture with pore sizes from sub-micrometer to several micrometers [13,23].

Until now, the studies of 3D graphene/polymer composites are mainly about 3D graphene/epoxy composites and 3D graphene/polydimethylsiloxane (PDMS) composites, etc. For example, Tang et al. prepared 3D graphene aerogel by in-situ reduction-assembly method. Epoxy/aerogel composites were synthesized by vacuum-assisted impregnation process. The composite exhibited good electrical conductivity and compressive properties [10]. Jia et al. prepared cellular-structured GF/epoxy composites. The

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composite was prepared by infiltrating epoxy into the porous GF which is grown on a Ni foam template via chemical vapor deposition. The results indicated that the addition of a small amount of 3D graphene foam makes the glass transition temperature of composite significantly higher than pure epoxy, and achieved significant improvements in both modulus/strength and fracture toughness [18]. Jun et al. used GO solutions to produce 3D reduced graphene oxide foam. 3D graphene/PDMS composites were prepared by vacuum-assisted impregnation process, which exhibited good electrical conductivity of about 3.2 S/m at a low loading of 1.9 wt% [17]. Zhao et al. prepared 3D GF grown on a Ni foam template via chemical vapor deposition. 3D graphene/PDMS composites were prepared by dropping liquid PDMS to the GF. The thermal resistance of GF/PDMS composite is only 14 mm^2 K/W [8]. The above results clearly indicate that the reinforcement with 3D graphene is effective in improving thermal, electrical and mechanical properties of composites. Current studies are mainly about using 3D graphene aerogel or GF to prepare 3D graphene/polymer composites. However, in the process of using freeze-drying to prepare graphene aerogel and especially in the process of impregnating 3D graphene with resin, it will cause more or less damage to the prepared 3D graphene structure. To avoid these problems, direct use of graphene hydrogels (GHs) to prepare 3D graphene/polymer composites is an effective way. And currently, composites prepared via graphene hydrogels are not reported and should be further investigated.

In this paper, a 3D graphene/phenolic resin (3DGP) composite was prepared via in-situ polymerization in GH. Hydrothermal method was used to produce GH. The scheme for preparing the 3DGP composite is shown in Fig. 1. The prepared GH which is hydrophobic (lipophilic) is directly immersed in the phenolic resin monomer solution to diffuse some monomers into the GH. After pre-curing, the phenolic resin monomers transform to water-soluble and non-volatile resole resin. In order to replace the water in the hydrogel with resole resin, evaporating water from the GH

by heating the mixture in the appropriate temperature. With the water left, there will be more and more resole resin immersed in the GH. Finally the purpose of utilizing phenolic resin to perfectly replace the water in the GH is achieved. The 3DGP composite was then synthesized by in-situ polymerization. The composites prepared by this method can retain the complete 3D network structure to achieve good dispersion of graphene sheets, and form 3D conducting network in polymer. Meanwhile, this composite was characterized in terms of mechanical and electrical properties. It shows good performance in both mechanical and electrical properties.

2. Experimental

2.1. Materials

Graphene oxide was supplied by Tangshan Jianhua Technology Development Co. Ltd. Ammonia (25%) and sodium hydroxide (96%) were purchased from Tianjin Kay Tong Chemical Reagent Co. Ltd. Iron acetate (95%) was bought from Meryer (Shanghai) Chemical Technology Co. Ltd. Formaldehyde solution (37%) was obtained from Tianjin Zhiyuan Reagent Co. Ltd. Phenol (AR) was purchased from Tianjin Hengxing Chemical Reagent Co. Ltd.

2.2. Preparation of GHs

The GH was synthesized by hydrothermal assembly of GO. 30 ml deionized water and a certain quality of GO (60, 90, 120, 150 mg) were added in a beaker, respectively. Then, the mixed solution was ultrasonicated for 100 min in ice-water bath to obtain GO suspension (2, 3, 4, 5 mg/ml). Then 5 mg of iron acetate (reducing agent) was added to the mixed solution. After that, the mixed solution was ultrasonicated for another 20 min. The mixed solution was then adjusted to pH 10 using ammonia. The mixture was then
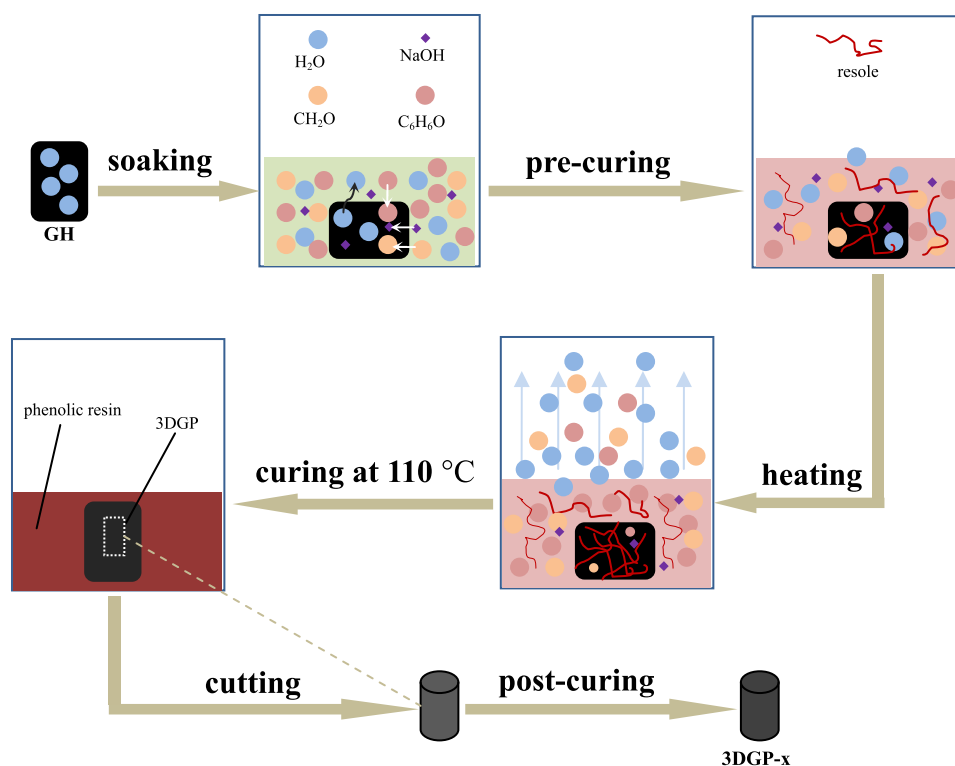

Fig. 1. Scheme for synthesis of 3DGP composites.