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Bio-inspired design and fabrication of an ultralight and strong nano-carbon gradient composite

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ABSTRACT

A nano-carbon composite, consisting of a graphene aerogel-carbon nanotube (CNT) film, is constructed by coating a strong and flexible CNT film onto the surface of a porous graphene aerogel core. The prepared gradient composite, ultralight and strong, can carry objects more than 15,000 times its own weight, exhibiting impressive compression resistance. Compared to the original graphene aerogel, the composite exhibits 8–9-fold increased values in its elastic modulus and compressive strength at a strain of 20% and an approximately 10-fold increase in electrical conductivities in the axial direction. In addition, the elastic recovery ability after compressive deformation and the ability to preserve liquid are also improved.

1. Introduction

Graphene aerogel, a three-dimensional structure assembled by random graphene layers, has received considerable attention and exhibits great potential in many fields (e.g., water treatment, energy storage, and biological catalysts) due to its low density, high porosity and high special surface area [1–5]. However, the mechanical properties of graphene aerogels are always unsatisfactory due to their high porosity. For example, the compressive strength and compressive modulus for low-density graphene aerogels (approximately 10 mg cm^{-3}) are usually on the order of 10^{-3}–10^{-2} MPa and 10^{-4}–10^{-1} MPa [6–9], although much better mechanical properties have been reported for graphene aerogels with higher densities (e.g., a Young's modulus of 300–1000 MPa for chemically cross-linked graphene aerogels with a density of approximately 200 mg cm^{-3}) [10,11]. Thus, enhancing the mechanical properties of graphene aerogels to realize their wide application has become a research focus in recent years. Many effective approaches have been presented, such as incorporating polymers into aerogels [12–14], chemical treatment [15–17], and preparing graphene/carbon nanotube (CNT) hybrid aerogels [18]. For example, Hong et al. increased the compressive strength and modulus of graphene aerogels from 21 kPa and 91.4 kPa to 182 kPa and 168.6 kPa, respectively, by cross-linking aerogels with PVA [19]. Moreover, Worsley et al. fabricated chemically cross-linked graphene aerogels with a density of 80–100 mg cm^{-3}, which exhibits super-compressive behaviour with a Young's modulus of approximately 50 MPa, failure strains of approximately 60% and a complete recovery for lower strains [11]. By creating hybrid materials with CNTs, Sui et al. enhanced the compressive modulus of the graphene/CNT aerogel to 2.9 MPa [18]. Despite the achievements in the previous methods, which mostly are chemical methods or involve incorporating other fillers, the improvement induced by the design of new structures has been rarely reported.

The porous core-dense skin structure is quite common in certain biological organs, including insect legs, as well as plant stems and branches. For example, the protection from a tough and strong skin outside the soft and porous inner core of stems and branches results in remarkable mechanically strengthened structures. The combined structure guarantees effective nutrient transportation, as well as necessary protection and support [20–22]. Furthermore, a similar concept of improving the mechanical properties of a low-density porous material by coating it with a stiffer and stronger skin layer has been commonly used in engineering, such as the cork sandwich structure, honeycomb sandwich structure and foam sandwich structure [23–25]. Inspired by these examples, the mechanical properties of graphene aerogels are significantly enhanced by designing a lightweight nano-carbon gradient composite with a porous graphene aerogel core and a tough, strong CNT film as the coating layer. An aligned CNT film drawn from a CNT

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array exhibits excellent mechanical tensile and functional properties [26,27] and has been successfully used in many areas, such as mechanical enhancement, optoelectronic devices, and energy devices [28,29]. More importantly, the strong and light CNT film does not cause a significant increase in the composite density, making it an ideal choice for the skin material.

In this work, for the first time, a "core-skin" nano-carbon gradient composite is designed and fabricated using an aligned CNT film and graphene aerogel. The graphene aerogel-CNT film composite exhibits substantially improved mechanical, electrical and liquid preserving features compared to the pristine graphene aerogel. Moreover, the mechanical strengthening characteristics of the gradient composite are analysed, which provides a design principle to enhance the mechanical properties of graphene aerogels.

2. Materials and methods

2.1. Materials

Expanded graphite (CX-200) was purchased from Qingdao Tianheda Graphite Co., Ltd. L-ascorbic acid (L-AA, AR) and polyvinyl alcohol (PVA) were purchased from Shanghai Aladdin Co., Ltd. Epoxy resin used in the experiment was bisphenol A type.

2.2. Preparation of graphene aerogels

As shown in Fig. 1a, the porous graphene aerogels were self-assembled by the sol-gel method, with the graphene layers being physically cross-linked inside. Large graphene oxide (GO) sheets were synthesized from the expanded graphite by a modified Hummers' method. A GO aqueous suspension (4 mg mL^{-1}) was prepared by ultrasonication (120 min under 90 W sonication with a KQ-400 KDE Digital Sonifier). Next, the L-AA solution is added into the GO suspension with a controlled weight ratio of 1:5 (GO: L-AA) to obtain a homogeneous suspension. The suspension is stirred ultrasonically for 10 min (90 W) before being kept in a water bath at 50 °C for 10 h to obtain the reduced graphene oxide (rGO) hydrogel precursor. After that, the rGO hydrogel was submerged in ethanol with magnetic stirring for seven days for solvent replacement, and then dried by supercritical CO_2 to obtain the graphene aerogel.

2.3. Preparation of graphene aerogel-CNT film composite

The spinnable CNT array used in the experiments was synthesized in a 5 in. quartz tube at 750 °C by chemical vapor deposition. The catalyst was prepared by depositing an alumina layer (30 nm)/iron layer (1 nm) on a silicon substrate with a thermal oxide layer by electron-beam evaporation. Argon with 6% hydrogen was used as the forming gas, and pure ethylene was used as the carbon source. The total flow rate of gases was set at 1.5 L min^{-1}. The nanotubes are approximately 200 μm in length, 3–5 nm in diameter and have 3–5 walls (Fig. 1b). As reported previously [30], due to the van der Waals force between the nanotubes, the CNTs could be drawn from the spinnable array continuously to obtain a CNT film [31]. In addition, this unique dry-drawing process allows a single layer CNT film to wrap closely around the aerogel core. By using motorized winding to wrap the CNT film hundreds of times around the aerogel core, the graphene aerogel-CNT film gradient composite can be fabricated simply and conveniently. Moreover, with different aerogel cores, the composites can be prepared in various sizes and shapes. Due to the effect of liquid surface tension and capillary force, neighbouring nanotubes can be squeezed closely together during solvent evaporation. Therefore, a solvent such as ethanol, a 1 wt% PVA/water solution or an epoxy/acetone solution were sprayed onto the film surface for densification during the winding of the CNT film. After winding, the composites were placed in a vacuum oven at 70 °C for 6 h for drying (when sprayed with PVA solution) or curing (when sprayed with epoxy solution).

The CNT film densified with ethanol was referred to as a pure CNT film, and the film densified with the PVA/water solution or epoxy/acetone solution were denoted as the CNT/PVA film or CNT/epoxy film, respectively. As for gradient composites, the graphene aerogel wrapped with the pure CNT film is denoted as the "graphene aerogel-pure CNT film"; the graphene aerogel wrapped with the CNT/PVA film is denoted as the "graphene aerogel-CNT/PVA film"; and the graphene aerogel wrapped with the CNT/epoxy film is donated as the "graphene aerogel-CNT/epoxy film".

2.4. Characterization of graphene aerogels and graphene aerogel-CNT film composite

The samples were weighed using an analytical balance by Sartorius Group (d = 0.01 mg). Each sample was weighed five times to calculate an average. The diameter and height of the samples were measured by a vernier caliper at five different positions to obtain an average value. The diameters are approximately 10 mm and the heights are approximately 8–10 mm. Density can be calculated by dividing mass by volume.

The quasi-static contact angle was tested by a contact angle measuring system OCA20 at room temperature. The testing liquid was deionized water. For each sample, five pictures at different positions were taken to calculate the average quasi-static contact angle. The compressive and cyclic compressive tests were carried out on a mechanical testing machine (Instron 3365) with a displacement rate of 1 mm min^{-1}. Five samples were tested each time, but the aerogel samples commonly showed fluctuations in their density and properties even though they were fabricated under the same conditions; this also holds true for the composite samples. In the following sections, even though all tested samples showed similar significant changes, only a typical set of test results is presented for more concise comparison. The electrical conductivity of the materials was calculated with the sheet resistance, which is tested by a four probe testing system ST-2258A. A scanning electron

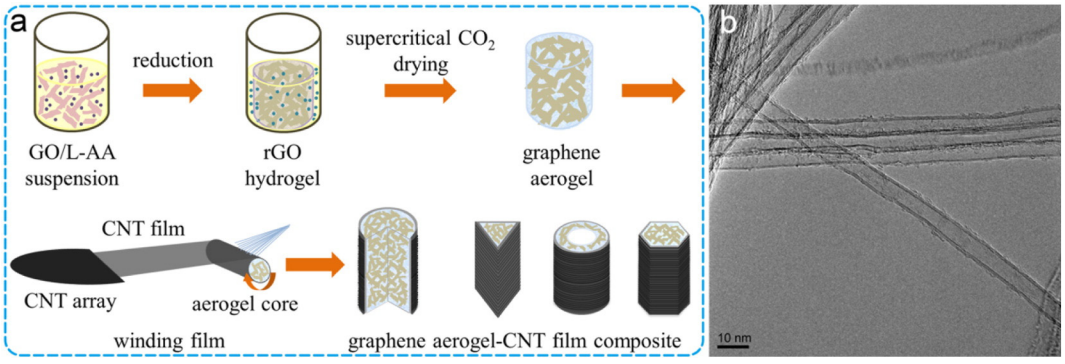

Fig. 1. (a) The schematic diagram showing the fabrication of the gradient composite. (b) A TEM image of the CNTs used in this work.